



# **San Joaquin Valleywide Air Pollution Study Agency**

**Sacramento, California**

## **Contributions of Chemical Constituents to Visibility Reduction During the California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study Final Report**

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**Contributions of Chemical Constituents to Visibility Reduction During the  
California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study**

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## EXECUTIVE SUMMARY

The purpose of the work described in this report is to characterize the contributions of atmospheric chemical constituents to visibility reduction during the California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study (CRPAQS). The objectives of this characterization were to answer the following questions:

Where, how much, how long, and how often do different chemical constituents (including liquid water) contribute to different levels of visibility reduction? How do chemical constituents contribute to the light extinction budget?

What are the sources of summertime light extinction in the Mojave Desert? How much of it is due to local, central California, and Southern California sources? How much is due to secondary and primary aerosols? How much is due to different source types, and how does this vary day-to-day and by time of day? What is the effect of removing different chemical constituents and source contributions from the light extinction budget?

Visibility reduction in these analyses was characterized by the light extinction coefficient ( $b_{\text{ext}}$ ), which is the fractional reduction in light intensity per unit path length of atmosphere. It is expressed in units of inverse megameters ( $\text{Mm}^{-1}$ ). Light extinction is caused by scattering and absorption of light by particles and gases in the atmosphere, and the light extinction coefficient is the sum of the light scattering and light absorption coefficients.

The contributions of individual atmospheric chemical constituents, which included ammonium nitrate, organic compounds, elemental carbon, ammonium sulfate and fine soil, were estimated through the use of constituent-specific light extinction efficiencies, which are the light scattering or light absorption coefficients resulting from unit concentrations of the constituents in the atmosphere. The light extinction efficiencies are in units of square meters per gram ( $\text{m}^2/\text{g}$ ), and the concentrations are in units of micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ). Concentrations of the chemical constituents were calculated from particulate matter chemical composition data. This approach has been used extensively for sites throughout the United States for the Interagency Monitoring of Protected Visual Environments (IMPROVE) program as well as for data collected in the San Joaquin Valley during IMS95.

The light extinction efficiencies used for IMS95 and the IMPROVE program, which are not the same, were evaluated for use in these analyses. Both sets of light extinction efficiencies are based on the assumption that ammonium nitrate, organic compounds, ammonium sulfate and fine soil scatter, but do not absorb, light. Thus, the light extinction efficiencies for these constituents

are light scattering efficiencies. The light scattering efficiencies for ammonium nitrate and ammonium sulfate depend on relative humidity, because these constituents are hygroscopic and can absorb water from the atmosphere. These efficiencies increase rapidly with increasing relative humidity above about 80 percent. The organic compound light scattering efficiency used for IMS95 depends weakly on relative humidity, while the efficiency used for the IMPROVE program is independent of relative humidity.

The IMS95 and IMPROVE program light scattering efficiencies were evaluated by applying them to annual (February 2000 through January 2001) CRPAQS data from the Fresno First Street monitoring site and comparing the resulting 24-hour average light scattering coefficients, calculated as the sum of the contributions from individual chemical constituents, with 24-hour average measurements of the light scattering coefficient. Data from this site were used for the evaluation because it was the only site equipped with an open-air nephelometer to measure the light scattering coefficient at near-ambient relative humidity. Because nephelometers located at other CRPAQS sites used heaters to maintain the sample relative humidity below about 72 percent, their readings did not reflect the potential effects on the light scattering coefficient of the high relative humidity that occurred frequently during fall and winter in the Central Valley.

The 24-hour average light scattering coefficients calculated with both sets of light scattering efficiencies were highly correlated with each other and with the measured values. However, both sets of calculated values were lower than the measurements at higher values, and the values calculated using the IMS95 efficiencies were lower than the values calculated using the IMPROVE program efficiencies. An empirical adjustment to the relative humidity dependence of the IMPROVE program ammonium nitrate and ammonium sulfate light scattering efficiencies was developed from the data. Application of this adjustment improved the agreement between the calculated and measured values.

Light scattering coefficients calculated using the IMPROVE efficiencies with the adjusted relative humidity dependence were compared with measurements made at three Mojave Desert and 10 non-desert sites with the heated nephelometers. Measured 24-hour average values agreed fairly well with values calculated using the nephelometer sample relative humidity at the non-Mojave Desert sites, which suggests that the use of the IMPROVE particle light scattering efficiencies with the adjusted relative humidity dependence can reproduce measured particle light scattering at sites in addition to the Fresno First Street site. However, the agreement was poor at the Mojave Desert sites. Examination of chemical composition data from these desert sites indicated that the sum of the chemical constituent concentrations frequently exceeded the measured  $PM_{2.5}$  mass concentration, which suggests that problems with the chemical composition measurements caused the poor agreement between the calculated and measured light scattering coefficients. Therefore, chemical constituent contributions to the light extinction coefficient at Mojave Desert sites were not estimated.

The IMPROVE program light extinction efficiencies with the adjusted relative humidity dependence were applied to data from 12 sites with annual ambient relative humidity and 24-hour average PM<sub>2.5</sub> chemical composition data. These sites were located in Sacramento, Stockton, Modesto, Merced, Fresno (three sites), Selma, Visalia, Oildale and Bakersfield (two sites). The resulting calculated 24-hour average light extinction coefficients and chemical constituent contributions were characterized to answer the following subsets of the first question posed above:

1. Where, how much and how often do individual constituents contribute to the light extinction coefficient?
2. How does the light extinction coefficient vary during the year?
3. When during the year do individual constituents contribute to the light extinction coefficient?

Additionally, the light extinction efficiencies were applied to chemical composition data from PM<sub>2.5</sub> samples that were collected during five daily time periods (0000-0500, 0500-1000, 1000-1300, 1300-1600 and 1600-2400) at sites in Bakersfield, Fresno and Angiola during four intensive operational periods (IOPs) that occurred between December 15, 2000 and February 3, 2001. The resulting contributions were used to characterize variations in chemical constituent contributions during the day.

**Where, how much and how often do individual constituents contribute to the light extinction coefficient?**

This question was addressed separately for days with high, low and intermediate 24-hour average light extinction. High and low light extinction days were defined as the days with the 20 percent highest and 20 percent lowest calculated light extinction coefficient at each site, and intermediate light extinction days were defined as the other 60 percent of the days. The average light extinction coefficient and chemical constituent contributions were calculated for the days in each of these categories to assess where and how much individual constituents contributed to the light extinction coefficient. Additionally, the frequency with which the chemical constituents contributed to the light extinction coefficient was examined to address how often the constituents contributed to the light extinction coefficient.

The average light extinction coefficient was lowest at Sacramento during all three categories of days. It was highest at Oildale during the 20 percent highest days and at Visalia during the middle 60 percent and 20 percent lowest days.

Ammonium nitrate was the largest contributor to the average light extinction coefficient at all sites during the 20 percent highest and middle 60 percent days. The large ammonium nitrate contribution during the 20 percent highest days was caused by high relative humidity as well as high ammonium nitrate concentrations. During the middle 60 percent days, organic compound concentrations were higher than ammonium nitrate concentrations, but elevated relative humidity caused the ammonium nitrate contribution to the light extinction coefficient to exceed the organic compound contribution. Organic compounds were the second-largest contributor during the 20 percent highest and middle 60 percent days and the largest contributor during the 20 percent lowest days. Average organic compound contributions were higher at the three Fresno sites than at the other sites.

Water, primarily associated with ammonium nitrate, contributed more than 60 percent of the average calculated light extinction coefficient during the 20 percent highest days at every site and more than 80 percent at Oildale. It accounted for more than 40 percent of the average calculated light extinction coefficient during the middle 60 percent days at all sites and over 60 percent of the light extinction coefficient at Visalia. During the 20 percent lowest days, it accounted for less than 25 percent of the calculated light extinction coefficient at many sites and no more than 40 percent at any site.

Ammonium nitrate frequently dominated the calculated light extinction coefficient on the 20 percent highest days, accounting for more than half of the light extinction on almost all of these days and frequently contributing more than 70 percent. It also accounted for more than half the 24-hour average light extinction coefficient on 10 to 40 percent of the middle 60 percent light extinction days. It only accounted for more than 50 percent on a few of the lowest 20 percent days at three sites.

Organic compounds occasionally accounted for 25 to 50 percent of the light extinction coefficient during the 20 percent highest days at Sacramento and the Fresno sites. It accounted for 25 to 50 percent of the light extinction during 20 to 50 percent of the middle 60 percent days and during 40 to 100 percent of the 20 percent lowest days.

Elemental carbon and ammonium sulfate usually accounted for less than 25 percent of the 24-hour average calculated light extinction coefficient.

Associations between high values of the light extinction coefficient and exceedances of the 24-hour  $PM_{2.5}$  NAAQS were also examined. The purpose of this examination was to evaluate how often measured  $PM_{2.5}$  mass concentrations exceeded the NAAQS of  $65 \mu g/m^3$  on the days with the 20 percent highest light extinction coefficient. The measured  $PM_{2.5}$  mass concentration was above the NAAQS on less than half of these days at the northern sites (Sacramento, Stockton, Modesto and Merced), while it was above the NAAQS on more than half of these days at the

southern sites (the three Fresno sites, Selma, Visalia, Oildale and the two Bakersfield sites). The average calculated light extinction coefficient was 1.9 to 2.5 times higher at the northern sites when the NAAQS was exceeded on the 20 percent highest light extinction coefficient days than when it was not. At most of the more southern sites, the calculated light extinction coefficient was less than twice as high when the NAAQS was exceeded on the 20 percent highest days than when it was not. Thus,  $PM_{2.5}$  concentrations were below the NAAQS on some days with poor visibility at all of the sites, but the frequency of days with poor visibility and  $PM_{2.5}$  concentrations below the NAAQS varied by site.

### **How does the light extinction coefficient vary during the year?**

The highest 24-hour average values of the light extinction coefficient during the year occurred during January, November and December at all sites, although low values also occurred during these months. High values also occurred during October at the Fresno and Visalia sites. The calculated light extinction coefficient was generally low from April through September.

### **When during the year do individual constituents contribute to the light extinction coefficient?**

Monthly average ammonium nitrate contributions were higher during January, February, November and December than during other months at all sites. The highest average contributions from organic compounds also occurred during January, November and December, particularly at Sacramento and the Fresno sites. Ammonium nitrate was the largest contributor to the monthly average light extinction coefficient during January, November and December at all sites as well as during March and October at some sites. Organic compounds were the largest contributor at most sites from April through September.

### **When and how long during the day do individual constituents contribute to the light extinction coefficient?**

The light extinction coefficient during the IOPs was usually highest during the nighttime sampling periods (1600-2400 and 0000-0500) and lowest during the afternoon sampling period (1300-1600), although the calculated light extinction coefficient remained high throughout the day at times at Bakersfield. Ammonium nitrate was the largest contributor during all sampling periods at Bakersfield and Angiola, while organic compounds plus elemental carbon were often the largest contributor at Fresno, particularly during the nighttime periods. Although the ammonium nitrate concentration was frequently higher during the morning (1000-1600) and afternoon sampling periods than at night, lower relative humidity during the afternoon than at night frequently led to low afternoon contributions to the light extinction coefficient.

## 1.0 INTRODUCTION

The California Regional PM<sub>10</sub>/PM<sub>2.5</sub> Air Quality Study (CRPAQS) is a multi-year program of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling. CRPAQS objectives are to: 1) provide an improved understanding of emissions and dynamic atmospheric processes that influence particle formation and distribution; 2) develop and demonstrate methods useful to decision makers in formulating and comparing candidate control strategies for attaining the federal and State PM<sub>10</sub>/PM<sub>2.5</sub> standards in central California; and 3) provide reliable means for estimating the impacts of control strategy options developed for PM<sub>10</sub>/PM<sub>2.5</sub> on visibility, air toxics, and acidic aerosols and on attainment strategies for other regulated pollutants, notably ozone.

CRPAQS is composed of three phases: 1) planning and basic research; 2) field programs; and 3) modeling and data analysis. The planning phase began in 1993 and was completed at the end of 1999. Planning activities included technical support studies to address key planning issues, demonstration studies of possible control techniques, a pilot study conducted during winter 1995/96, known as the 1995 Integrated Monitoring Study (IMS95), preliminary modeling, and development of detailed plans for each of the subsequent Study components.

The field programs phase of the Study consisted of 14 months of monitoring throughout the San Joaquin Valley (SVJ) and surrounding regions, as well as intensive monitoring during fall- and winter-like conditions when PM<sub>10</sub> and PM<sub>2.5</sub> concentrations are highest. Air quality sampling locations in the annual network (December 1, 1999, through January 31, 2001) consisted of a combination of "anchor" monitoring sites measuring both gaseous and aerosol species, "satellite" sites measuring aerosol species using portable filter samplers and nephelometers, and a "backbone" network of Air Resources Board (ARB) and air pollution control district sites.

The CRPAQS winter episodic field study took place over a period of eight weeks on a forecast basis from December 1, 2000 through February 3, 2001. Special emphasis was placed on collection of continuous and species-specific particulate measurements to support both receptor and grid-based modeling approaches. Fifteen episode days were selected by forecast for additional monitoring to characterize the evolution of PM<sub>2.5</sub> episodes.

A summer study extended monitoring into the Mojave desert to better understand transport from the San Joaquin Valley to the desert and the contributions to summertime haze in that region. Additional satellite sites were located along transport pathways and an anchor site was established at Edwards Air Force Base (AFB).

The purpose of the work described in this report is to characterize the contribution of atmospheric chemical constituents to visibility reduction at CRPAQS sites. The objectives of this characterization were to answer the following questions:



Where, how much, how long, and how often do different chemical constituents (including liquid water) contribute to different levels of visibility reduction? How do chemical constituents contribute to the light extinction budget?

What are the sources of summertime light extinction in the Mojave Desert? How much of it is due to local, central California, and Southern California sources? How much is due to secondary and primary aerosols? How much is due to different source types, and how does this vary day-to-day and by time of day? What is the effect of removing different chemical constituents and source contributions from the light extinction budget?

Visibility reduction in these analyses was characterized by the light extinction coefficient ( $b_{\text{ext}}$ ), which is the fractional reduction in light intensity per unit path length of atmosphere. It is expressed in units of inverse megameters ( $\text{Mm}^{-1}$ ). Light extinction is caused by scattering and absorption of light by particles and gases in the atmosphere, and the light extinction coefficient is the sum of the light scattering and light absorption coefficients.

The contributions of individual atmospheric chemical constituents were estimated through the use of constituent-specific light extinction efficiencies, which are the light scattering or light absorption coefficients resulting from unit concentrations of the constituents in the atmosphere. The light extinction efficiencies are in units of square meters per gram ( $\text{m}^2/\text{g}$ ), and the concentrations are in units of micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ). The constituent concentrations were calculated from particulate matter chemical composition data. This approach has been used extensively for sites throughout the United States for the Interagency Monitoring of Protected Visual Environments (IMPROVE) program (Sisler and Malm, 2000) as well as for data collected in the San Joaquin Valley during IMS95 (McDade, 1997).

Section 2 of this report presents the approach to estimate chemical constituent contributions to the light extinction coefficient, including the calculation of constituent concentrations and the selection and evaluation of light extinction efficiencies. It also discusses potential problems with chemical composition data from the Mojave Desert sites that led to the conclusion that data from Mojave Desert sites could not be used to estimate constituent contributions to the light extinction coefficient. Therefore, this work did not attempt to address visibility reduction at Mojave Desert sites.

Section 3 presents and discusses the estimated chemical constituent contributions, and Section 4 provides a summary of the results.



## 2.0 APPROACH

The chemical constituents in the analyses included ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), organic compounds (OCM), elemental carbon (EC), ammonium sulfate  $[(\text{NH}_4)_2\text{SO}_4]$  and fine soil in particles smaller than 2.5 microns ( $\mu\text{m}$ ) aerodynamic diameter. In addition to these constituents, the IMPROVE program (Sisler and Malm, 2000) and IMS95 analyses (McDade, 1997) also included the contribution from light scattering by coarse particles (particles with diameters between 2.5 and 10  $\mu\text{m}$ ). However,  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  mass concentrations, which are required to calculate coarse particle concentrations, were not measured routinely at most CRPAQS sites where  $\text{PM}_{2.5}$  chemical composition was measured. Therefore, contributions from light scattering by coarse particles were not included. However, the IMS95 analyses concluded that the contribution from coarse particles was less than a few percent when the extinction coefficient was high.

With the exception of elemental carbon, the chemical constituents were not measured directly. Instead, they were calculated from measured constituents using the approach from the IMS95 analyses as follows:

$$[\text{NH}_4\text{NO}_3] = 1.29 [\text{NO}_3^{-1}] \quad (2-1)$$

$$[\text{OCM}] = 1.4 [\text{OC}] \quad (2-2)$$

$$[(\text{NH}_4)_2\text{SO}_4] = 1.375 [\text{SO}_4^{2-}] \quad (2-3)$$

$$[\text{fine soil}] = 1.89 [\text{Al}] + 2.14 [\text{Si}] + 1.4 [\text{Ca}] + 1.43 [\text{Fe}] \quad (2-4)$$

where:

$[\text{NO}_3^{-1}]$  = measured nitrate concentration ( $\mu\text{g}/\text{m}^3$ )

$[\text{OC}]$  = measured organic carbon concentration ( $\mu\text{g}/\text{m}^3$ )

$[\text{SO}_4^{2-}]$  = measured sulfate concentration ( $\mu\text{g}/\text{m}^3$ )

$[\text{Al}]$  = measured aluminum concentration ( $\mu\text{g}/\text{m}^3$ )

$[\text{Si}]$  = measured aluminum concentration ( $\mu\text{g}/\text{m}^3$ )

$[\text{Ca}]$  = measured aluminum concentration ( $\mu\text{g}/\text{m}^3$ )

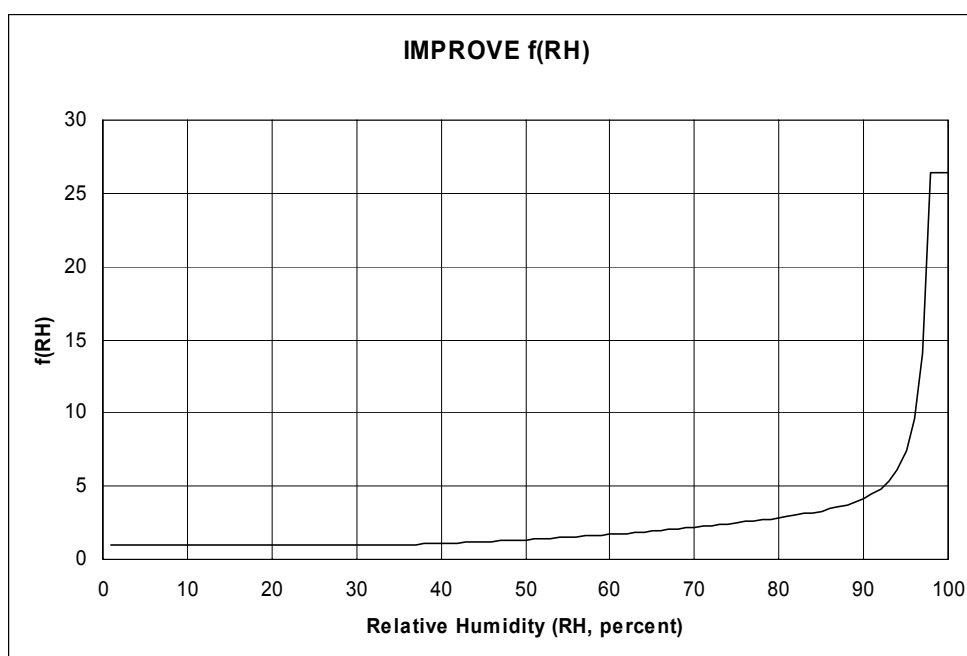
$[\text{Fe}]$  = measured aluminum concentration ( $\mu\text{g}/\text{m}^3$ )

Equations 2-1 and 2-3 assume that nitrate and sulfate are fully neutralized by ammonium. The factor of 1.4 in Equation 2-2 accounts for hydrogen, oxygen and other elements that may be associated with carbon in PM<sub>2.5</sub> organic compounds. Equation 2-4 assumes that the elements associated with fine soil are present as their oxides.

The IMS95 and IMPROVE program light extinction efficiencies, which are listed in Table 2-1, were evaluated for possible use in these analyses. As seen in the table, the IMS95 and IMPROVE program light scattering efficiencies for ammonium nitrate and ammonium sulfate depend on relative humidity to account for liquid water associated with these hygroscopic compounds. The IMS95 light scattering efficiency for organic compounds also depends on relative humidity, but the dependence is weaker (i.e., increasing relative humidity does not increase the light scattering efficiency as much as it does for ammonium sulfate and ammonium nitrate). Figure 2-1 shows the relative humidity dependence of the IMPROVE ammonium nitrate and ammonium sulfate light scattering efficiencies as presented by Lowenthal and Kumar (2003). As seen in the figure, the light scattering efficiency increases rapidly with increasing relative humidity above about 80 percent.

**Table 2-1**  
**IMS95 and IMPROVE Light Extinction Efficiencies**

Constituent	Light Extinction Efficiency (m <sup>2</sup> /g) <sup>a</sup>	
	IMS95	IMPROVE
Ammonium Nitrate	$2.1/(1-RH/100)^{0.7}$	3f(RH)
Ammonium Sulfate	$2.1/(1-RH/100)^{0.7}$	3f(RH)
Organic Compounds	$2.8/(1-RH/100)^{0.2}$	4
Elemental Carbon	10	10
Fine Soil	2	1
<sup>a</sup> RH = relative humidity (percent)		



**Figure 2-1. Dependence of IMPROVE Ammonium Nitrate and Ammonium Sulfate Light Scattering Efficiencies on Relative Humidity**

The elemental carbon light absorption efficiency was set to the  $10 \text{ m}^2/\text{g}$  value in Table 2-1 that was used for both IMS95 (McDade, 1997) and IMPROVE (Sisler and Malm, 2000).

The IMS95 and IMPROVE light scattering efficiencies were evaluated by applying them to CRPAQS data from the Fresno First Street monitoring site and comparing the calculated particle light scattering coefficient with measured values. Data from the Fresno First Street site were used because it was the only site with an Optec NGN-2 open-air nephelometer that measured the particle light scattering coefficient ( $b_{sp}$ ) at near-ambient relative humidity. The particle light scattering coefficient was also measured at other CRPAQS sites. However, these measurements were intended to provide an indication of the  $\text{PM}_{2.5}$  mass concentration. Because of the rapid increase in the ammonium nitrate and ammonium sulfate light scattering efficiencies with increasing relative humidity above about 70 percent, and the frequent occurrence of periods of high relative humidity in the Central Valley during the fall and winter, Radiance Research nephelometers equipped with heaters to maintain the sample relative humidity below about 72 percent were used at these sites. Therefore, these nephelometers could not be used to evaluate the ability of the light extinction efficiencies to reproduce the measured light scattering coefficient at elevated relative humidity.

The IMS95 and IMPROVE program light scattering efficiencies were applied to 24-hour average measured chemical constituent concentrations. Twenty-four hour average relative humidity, calculated as the average of hourly-average values, was used in the IMS95 ammonium nitrate, ammonium sulfate and organic compound light scattering efficiency calculations. Hourly values of

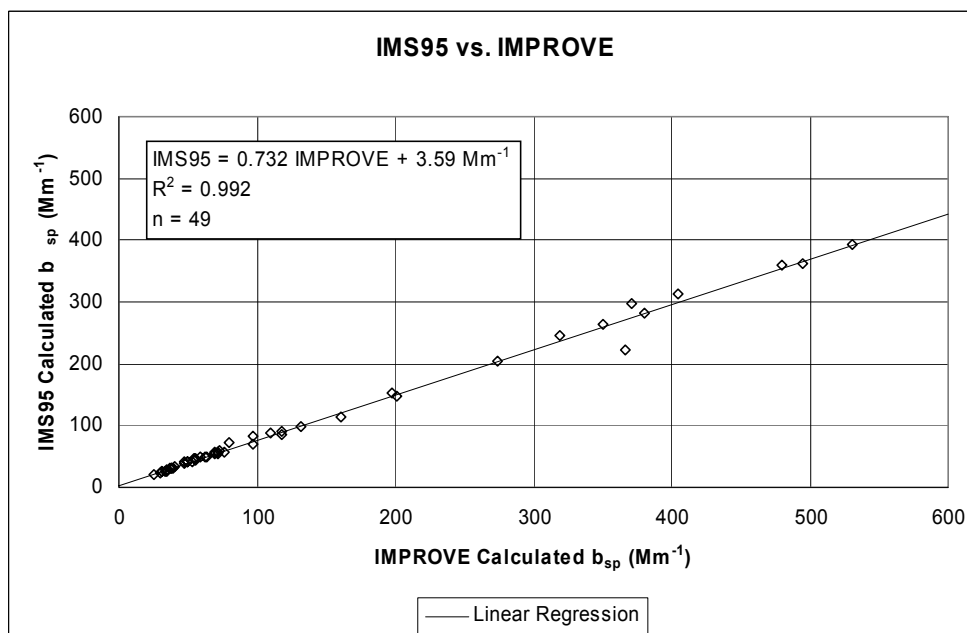
the IMPROVE program  $f(RH)$  function were calculated from hourly-average relative humidity and averaged over 24 hours to calculate the IMPROVE program ammonium nitrate and ammonium sulfate light scattering efficiencies. Hours with relative humidity above 95 percent were excluded from the calculation of 24-hour average relative humidity, IMPROVE  $f(RH)$ , and measured particle light scattering coefficient to avoid periods with fog. Days with less than 18 hours included in the 24-hour averages were excluded.

The minimum, average and maximum values of the measured 24-hour average particle light scattering coefficient, relative humidity, IMPROVE  $f(RH)$  and ammonium nitrate, organic compound, elemental carbon, ammonium sulfate and fine soil concentrations, calculated from the measured particulate matter chemical composition, are listed in Table 2-2.

**Table 2-2**  
**Summary of Data from Fresno First Street Site Used to Develop Light Extinction Efficiencies**

Quantity	Minimum <sup>a</sup>	Average <sup>a</sup>	Maximum <sup>a</sup>
Measured particle light scattering coefficient ( $Mm^{-1}$ )	26	226	1159
Relative Humidity (%)	32	57	82
IMPROVE $f(RH)$	1.06	1.97	3.24
Ammonium Nitrate ( $\mu g/m^3$ )	1.3	10.5	47.1
Organic Compounds ( $\mu g/m^3$ )	3.2	13.6	51.5
Elemental Carbon ( $\mu g/m^3$ )	0.3	2.8	10.3
Ammonium Sulfate ( $\mu g/m^3$ )	0.3	1.9	3.8
Fine Soil ( $\mu g/m^3$ )	0.1	1.2	9.7
<sup>a</sup> Based on 49 days			

Light scattering coefficients calculated from the IMS95 and IMPROVE program light scattering efficiencies are compared in Figure 2-2. Results using the IMS95 and IMPROVE program efficiencies are highly correlated, but the IMS95 efficiency results are about 73 percent of the IMPROVE program results.

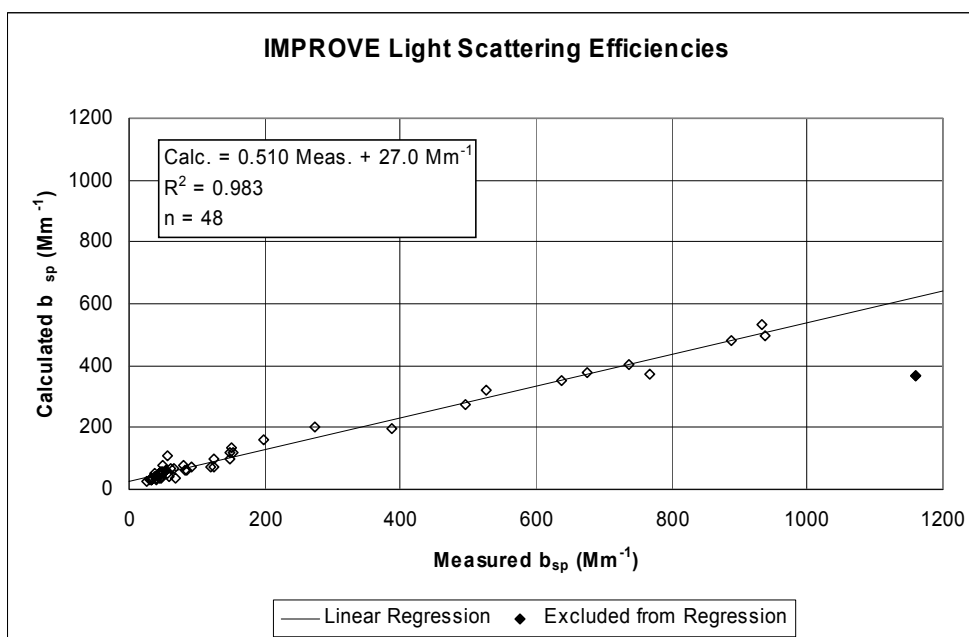


**Figure 2-2. Comparison of  $b_{sp}$  Calculated for the Fresno First Street Site Using IMS95 and IMPROVE Light Scattering Efficiencies**

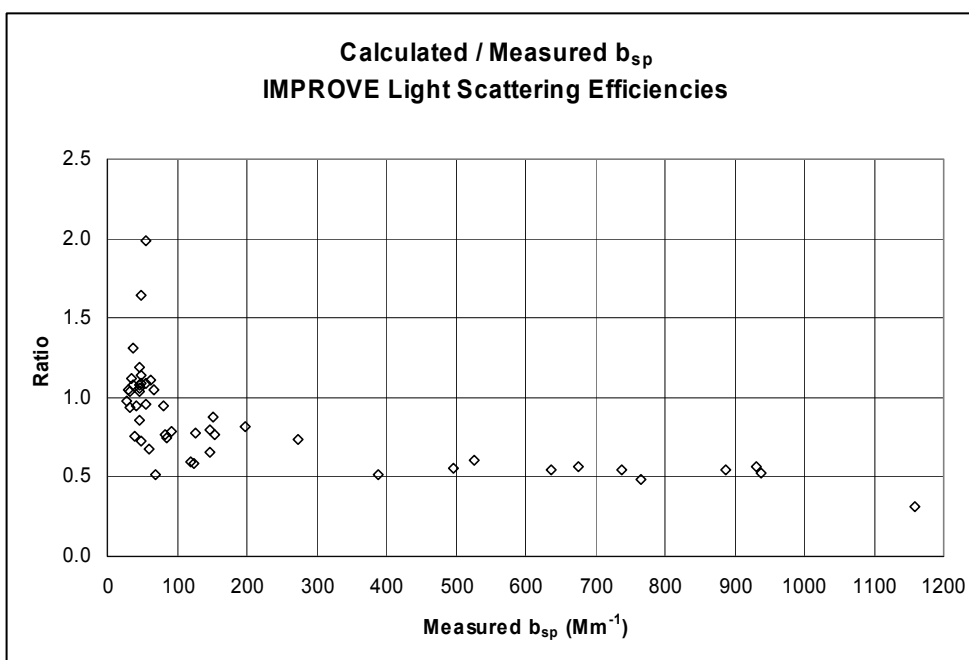
The light scattering coefficient calculated from the IMPROVE program light scattering efficiencies is compared with measured values in Figure 2-3. The correlation between the calculated and measured values is good ( $R^2 = 0.983$ ), but the measured values are higher than the calculated values, especially for measured values above about  $200 Mm^{-1}$ . This is further illustrated in Figure 2-4, which shows the ratio of the calculated and measured light scattering coefficient as a function of the measured values. As seen, the calculated light scattering coefficient is less than the measured coefficient for all measured values above about  $100 Mm^{-1}$ , but measured values are frequently lower than calculated values for measured values below about  $75 Mm^{-1}$ .

Because the light scattering coefficient calculated using the IMS95 light scattering efficiencies was lower than values calculated using the IMPROVE program efficiencies, the IMS95 efficiencies under-predict the coefficient even more than the IMPROVE program efficiencies. Therefore, the IMS95 light scattering efficiencies were not considered further for these analyses.

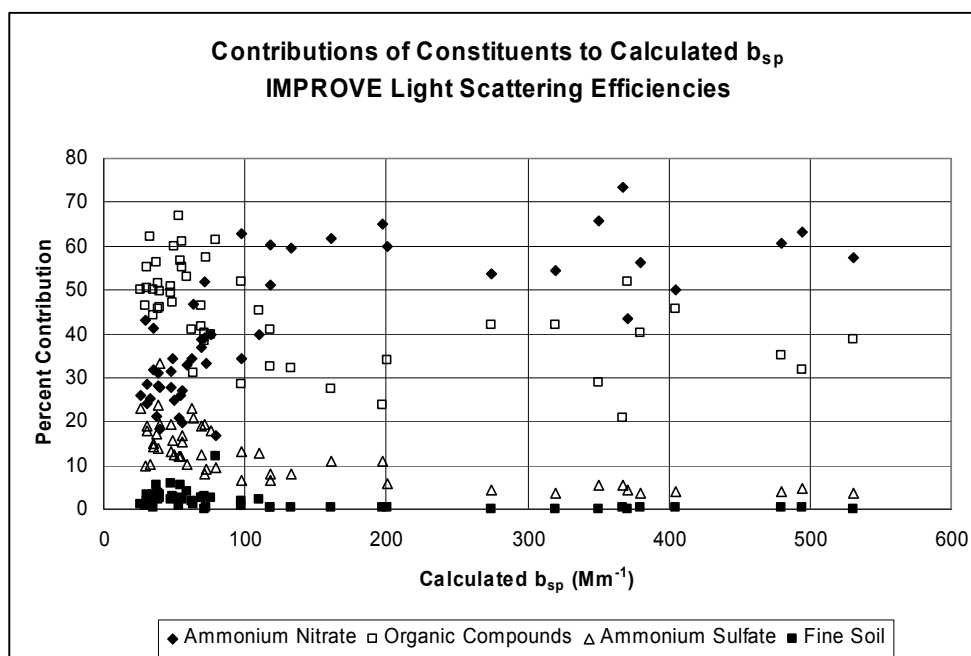
Possible causes for the underestimation of measured light scattering at high measured values and the overestimation at low measured values were investigated by first plotting the percentage contributions of chemical constituents to the calculated light scattering coefficient as a function of the calculated coefficient. As seen in Figure 2-5, ammonium nitrate and organic compounds are the major contributors to calculated  $b_{sp}$ . The ammonium nitrate contribution accounts for 50 percent or more of the calculated light extinction coefficient for all but one calculated value above  $100 Mm^{-1}$ , while organic compounds tend to be the largest contributor for calculated values below



**Figure 2-3. Comparison of  $b_{sp}$  Calculated for the Fresno First Street Site Using IMPROVE Light Scattering Efficiencies with Measured  $b_{sp}$**



**Figure 2-4. Ratio of  $b_{sp}$  Calculated for the Fresno First Street Site using IMPROVE Light Scattering Efficiencies to Measured  $b_{sp}$  as a Function of Measured  $b_{sp}$**



**Figure 2-5. Percentage Contributions of Chemical Constituents to Calculated  $b_{sp}$  for the Fresno First Street Site using IMPROVE Light Scattering Efficiencies as a Function of Measured  $b_{sp}$**

100  $Mm^{-1}$ . These results suggest that either the ammonium nitrate or the organic compound light scattering efficiencies may be underestimated at high values of the calculated light scattering coefficient and overestimated at low values.

Next, the ratio of the calculated to measured particle light scattering coefficient was plotted as a function of relative humidity. As seen in Figure 2-6, the under-prediction of the measured light scattering coefficient tends to be greater at higher relative humidity. This result, along with the large relative contribution of ammonium nitrate to the calculated particle light scattering coefficient at higher values, suggests that the IMPROVE light scattering efficiency for ammonium nitrate may not adequately account for the dependence on relative humidity.

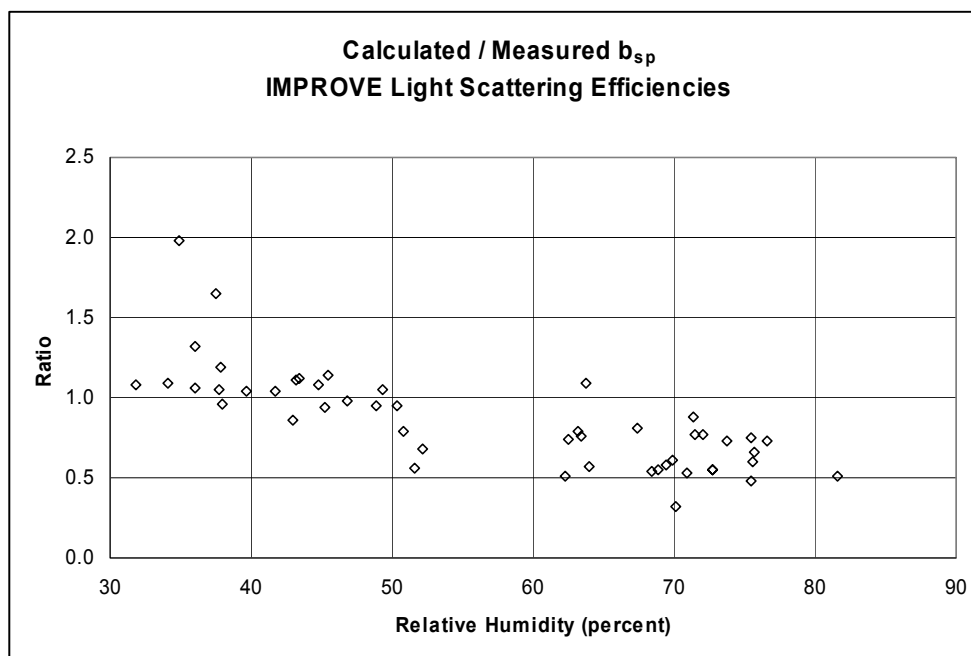
Values of an “apparent”  $f(RH)$  function,  $f(RH)'$ , were calculated from:

$$f(RH)' = (b_{sp,m} - 4[OCM] - 1 [fine soil]) / (3 [NH_4NO_3] + 3 [(NH_4)_2SO_4]) \quad (2-5)$$

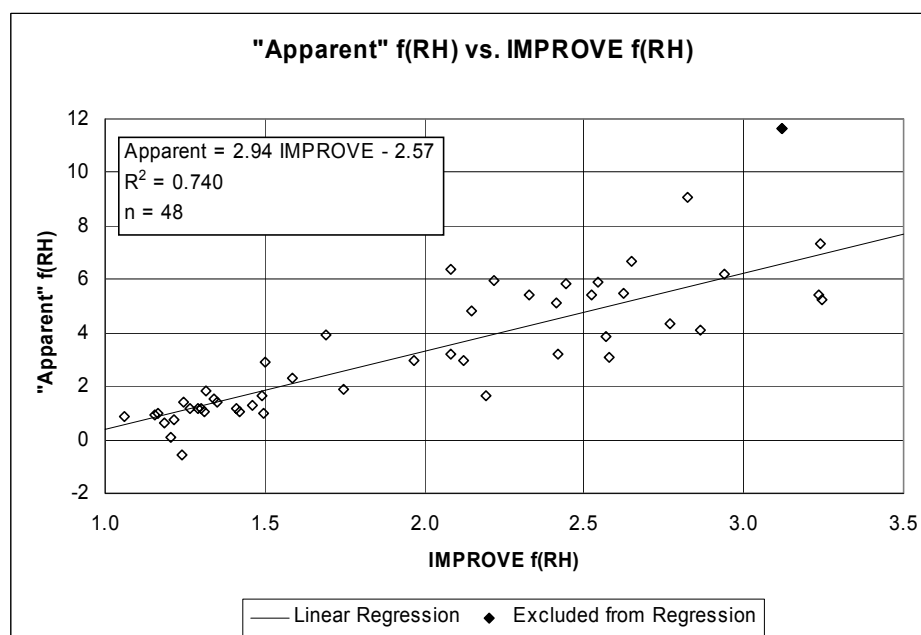
where  $b_{sp,m}$  is the measured particle light scattering coefficient.

Apparent  $f(RH)$  is plotted as a function of 24-hour average  $f(RH)$  in Figure 2-7. The correlation between the apparent and IMPROVE  $f(RH)$  is relatively strong ( $R^2 = 0.740$ ). The linear regression of apparent  $f(RH)$  as a function of IMPROVE  $f(RH)$  was used to calculate adjusted 24-hour average IMPROVE  $f(RH)$  values. The particle light scattering coefficient calculated using these adjusted  $f(RH)$  values is compared with the measured light scattering coefficient in Figure 2-8.

The use of the adjusted  $f(RH)$  values substantially improves the comparison, increasing the slope of the linear regression of calculated  $b_{sp}$  as a function of measured  $b_{sp}$  from 0.51 to 0.80.

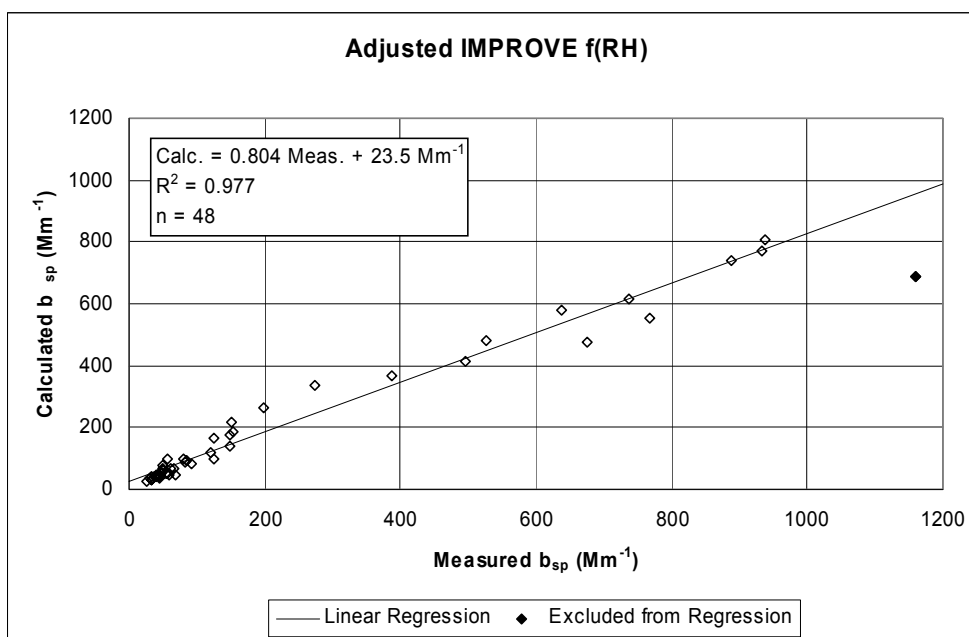


**Figure 2-6. Ratio of  $b_{sp}$  Calculated for the Fresno First Street Site using IMPROVE Light Scattering Efficiencies to Measured  $b_{sp}$  as a Function of Relative Humidity**



**Figure 2-7. Apparent  $f(RH)$  for the Fresno First Street Site as a Function of IMPROVE  $f(RH)$**

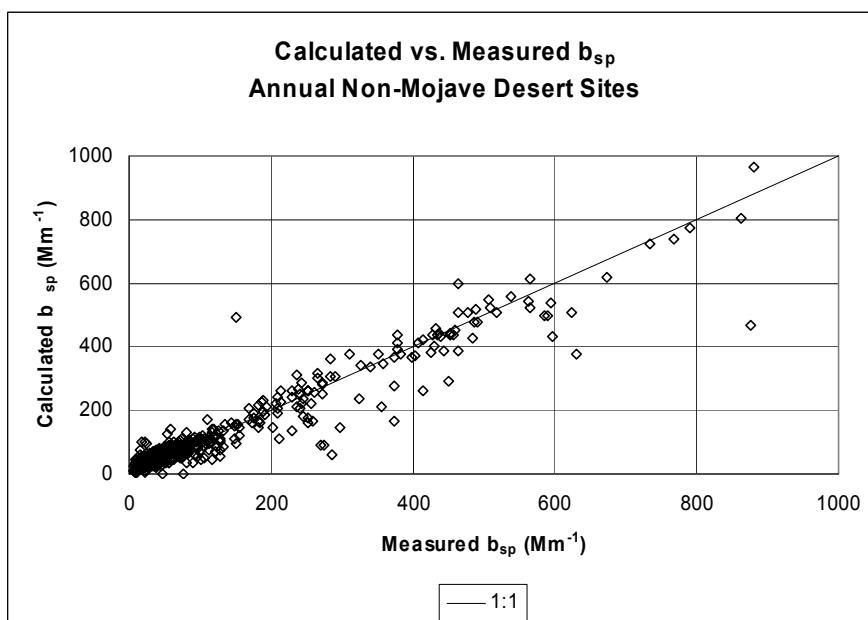




**Figure 2-8. Comparison of  $b_{sp}$  Calculated for the Fresno First Street Site Using IMPROVE Light Scattering Efficiencies and Adjusted  $f(RH)$  with Measured  $b_{sp}$**

The IMPROVE light scattering efficiencies with the adjusted  $f(RH)$  were applied to data from sites with concurrent annual particulate matter chemical composition and Radiance Research nephelometer data. Hourly  $f(RH)$  values were calculated from internal nephelometer relative humidity measurements, and the adjusted  $f(RH)$  was calculated from the 24-hour average  $f(RH)$ . The calculated 24-hour average particle light scattering coefficient is shown as a function of the 24-hour average measured particle light scattering coefficient in Figure 2-9 for all non-Mojave Desert sites. Although the measured particle light scattering coefficient exceeded the calculated coefficient for some days, most of the values tend to be close to the one-to-one line in the figure. This result suggests that the use of the IMPROVE program particle light scattering efficiencies with the adjusted  $f(RH)$  can reproduce measured particle light scattering at sites in addition to the Fresno First Street site.

Based on these comparisons, the IMPROVE program light extinction efficiencies with the adjusted  $f(RH)$  were used for the analyses presented in this report. These light extinction efficiencies are listed in Table 2-3 with the IMPROVE program and IMS95 efficiencies.

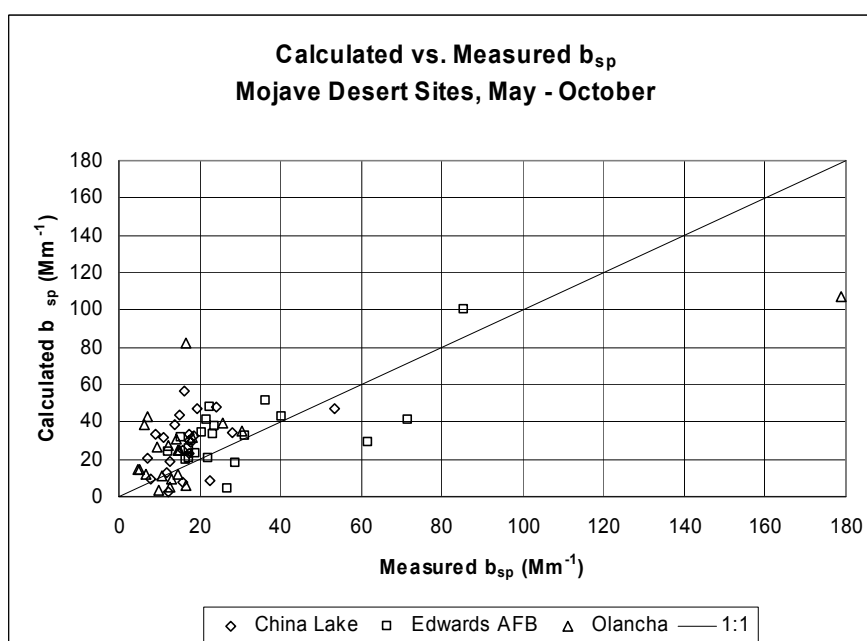


**Figure 2-9. Comparison of  $b_{sp}$  Calculated for Annual Non-Mojave Desert Sites Using IMPROVE Light Scattering Efficiencies and Adjusted  $f(RH)$  with  $b_{sp}$  Measured with Radiance Research Nephelometers**

**Table 2-3  
Light Extinction Efficiencies Used for This Work, IMPROVE and IMS95**

Constituent	Light Extinction Efficiency ( $m^2/g$ ) <sup>a</sup>		
	This Work	IMPROVE	IMS95
Ammonium Nitrate	$3[2.94f(RH)-2.57]$	$3f(RH)$	$2.1/(1-RH/100)^{0.7}$
Ammonium Sulfate	$3[2.94f(RH)-2.57]$	$3f(RH)$	$2.1/(1-RH/100)^{0.7}$
Organic Compounds	4	4	$2.8/(1-RH/100)^{0.2}$
Elemental Carbon	10	10	10
Fine Soil	1	1	2
<sup>a</sup> RH = relative humidity (percent)			

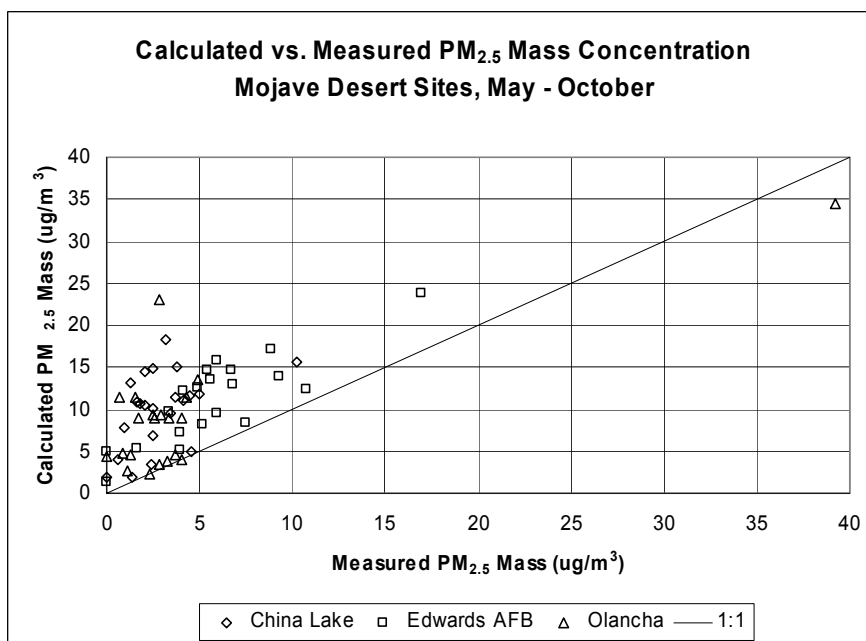
A similar comparison for measurements at the three Mojave Desert sites with concurrent particulate matter chemical composition and nephelometer data between May and October is shown in Figure 2-10. This time of the year was selected because mixing heights are higher than during the rest of the year, which increases the potential for transport from the San Joaquin Valley and South Coast Air Basin to the Desert. The agreement between calculated and measured particle light scattering coefficients is much poorer than for the non-Mojave Desert sites shown in Figure 2-9.



**Figure 2-10. Comparison of  $b_{sp}$  Calculated for Mojave Desert Sites between May and October Using IMPROVE Light Scattering Efficiencies and Adjusted  $f(RH)$  with  $b_{sp}$  Measured with Radiance Research Nephelometers**

This poor agreement at the Mojave Desert sites was probably caused by problems with the  $PM_{2.5}$  chemical composition measurements. Figure 2-11 shows the sum of the calculated chemical constituent concentrations as a function of measured  $PM_{2.5}$  mass concentration. As seen, the sum of the constituent concentrations frequently exceeded the measured mass concentration, particularly at lower values. Similar results were obtained with low mass concentration measurements for sites in the San Joaquin Valley (Magliano, 2005). According to Watson (2005), during summer, the reconstructed mass can be higher because: 1) the organic carbon is positively biased (at low levels the vapors absorbed by the quartz filter may make the organic carbon higher than it is); on the other hand, some of the particle organics may have evaporated from the Teflon filter making the mass lower than it should be; and 2) the self-absorption correction for Al and Si

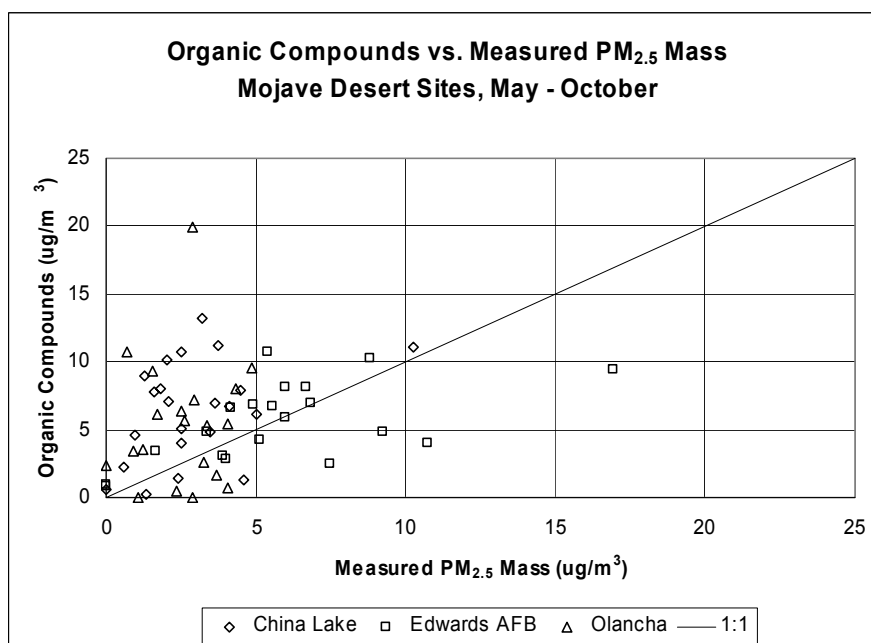
measurements by x-ray fluorescence may be larger than it should be for the size distribution (a nominal size distribution for the coarse soil particles is assumed; if they are actually smaller, then they do not absorb as much of the emitted x-rays and the values are over-corrected for the self-absorption).



**Figure 2-11. Comparison of Calculated and Measured PM<sub>2.5</sub> Mass Concentrations from May through October at Mojave Desert Sites**

Figure 2-12 shows the organic compound concentration calculated from reported organic carbon as a function of measured PM<sub>2.5</sub> mass for samples when the measured mass concentration was below 20 µg/m<sup>3</sup>. This figure shows that the calculated organic compound concentration frequently exceeded the measured PM<sub>2.5</sub> mass concentration, which is consistent with a positive artifact biasing the organic carbon measurements.

Because of the lack of agreement between calculated and measured PM<sub>2.5</sub> mass concentrations, chemical constituent contributions to the light extinction coefficient were not estimated for the Mojave Desert sites.



**Figure 2-12. Comparison of Calculated Organic Compound Concentration and Measured PM<sub>2.5</sub> Mass Concentrations from May through October at Mojave Desert Sites for Mass Concentrations below 25 µg/m<sup>3</sup>**

### **3.0 CHARACTERIZATION OF CONSTITUENT CONTRIBUTIONS TO LIGHT EXTINCTION**

This section presents analyses that were intended to answer the first question posed in Section 1:

Where, how much, how long, and how often do different chemical constituents (including liquid water) contribute to different levels of visibility reduction? How do chemical constituents contribute to the light extinction budget?

This question was divided into the following series of questions:

1. Where, how much and how often do individual constituents contribute to the light extinction coefficient?
2. How does the light extinction coefficient vary during the year?
3. When during the year do individual constituents contribute to the light extinction coefficient?
4. When and how long during the day do individual constituents contribute to the light extinction coefficient?

The next subsection describes how the light extinction efficiencies were applied to calculate chemical constituent contributions to the light extinction coefficient. The remaining subsections then present the analyses used to answer these four questions.

#### **3.1 Application of Light Extinction Efficiencies**

PM<sub>2.5</sub> samples were collected over 24-hour periods, from midnight to midnight, nominally every sixth day, from December 1999 through January 2001 at several non-Mojave Desert sites during CRPAQS. Concurrent relative humidity measurements were made at or near 13 of these sites, shown in Figure 3-1. Three of the sites were located in Fresno (First Street, Motor Vehicle and Residential) and two of the sites were located in Bakersfield (California Avenue and Residential). Single sites used in these analyses were located in Sacramento (T Street), Stockton (Hazelton Avenue), Modesto (14<sup>th</sup> Street), Merced (M Street), Selma (Airport), Visalia (Church Street), Angiola (4<sup>th</sup> Avenue) and Oildale (Manor Street). Descriptions of the sites and their surroundings can be found at:

<http://www.arb.ca.gov/airways/crpaqs/siteAtlas/siteatlas.htm>

The light extinction efficiencies were applied to 24-hour data from 12 of these 13 sites to characterize the magnitude and frequency of contributions of chemical constituents to the light

extinction coefficient by location and by time of year. Because complete data were only available for 28 days at the Angiola site, primarily due to entire days with relative humidity above 95 percent and to periods of missing relative humidity data, this site was not included in the analyses of 24-hour data. Table 3-1 lists the first and last sampling dates and the number of days included in the analyses for the 12 sites, as well as the relative-humidity monitoring location selected to represent each site.



**Figure 3-1. Monitoring Sites Used to Characterize Chemical Constituent Contributions to Light Extinction**



**Table 3-1**  
**Particulate Matter and Relative Humidity Monitoring Sites, First and Last Dates, and**  
**Number of Days Used for Analyses**

Site	Relative Humidity Site (Site Code)	First Date	Last Date	Number of Days
Sacramento	Sacramento T Street (S13)	12/2/99	1/31/01	69
Stockton	Stockton Hazelton (SOH)	12/14/99	1/31/01	59
Modesto	Modesto 2 Meter Height (MD2MH)	12/2/99	1/31/01	63
Merced	Merced 2 Meter Height (MERC2MH)	12/8/99	1/31/01	66
Fresno First Street	Fresno First Street (FSF)	12/2/99	1/31/01	66
Fresno Motor Vehicle	Fresno First Street (FSF)	12/8/99	1/31/01	67
Fresno Residential	Fresno First Street (FSF)	12/2/99	1/31/01	71
Selma	Fresno First Street (FSF)	12/2/99	1/31/01	69
Visalia	Visalia/ICI Americas 2 Meter Height (VLA2MH)	12/8/99	1/31/01	66
Oildale	Bakersfield California Avenue (BAC)	12/8/99	1/31/01	64
Bakersfield California Avenue	Bakersfield California Avenue (BAC)	12/8/99	1/31/01	62
Bakersfield Residential	Bakersfield California Avenue (BAC)	12/20/99	1/31/01	46

The light extinction efficiencies were applied to each day with available relative humidity and 24-hour average  $PM_{2.5}$  chemical composition data. Days with missing nitrate, organic carbon, elemental carbon, or sulfate were excluded. The adjusted IMPROVE  $f(RH)$  value was calculated from hourly-average relative humidity data. These values were averaged over the 24-hour particulate matter sampling periods. Hours with relative humidity above 95 percent were excluded to avoid periods of fog. The contribution of liquid water to the light extinction coefficient was estimated by subtracting the light extinction coefficient calculated with the relative humidity set to zero (a "dry" light extinction coefficient) from the light extinction coefficient calculated with the adjusted  $f(RH)$  corresponding to the ambient relative humidity.

$PM_{2.5}$  samples were collected daily during five time periods (0000-0500, 0500-1000, 1000-1300, 1300-1600 and 1600-2400) at the Bakersfield California Avenue, Fresno First Street and Angiola sites during four intensive operational periods (IOPs) that occurred between December 15, 2000 and February 3, 2001. The light extinction efficiencies were applied to these data to characterize variations in chemical constituent contributions during the day.

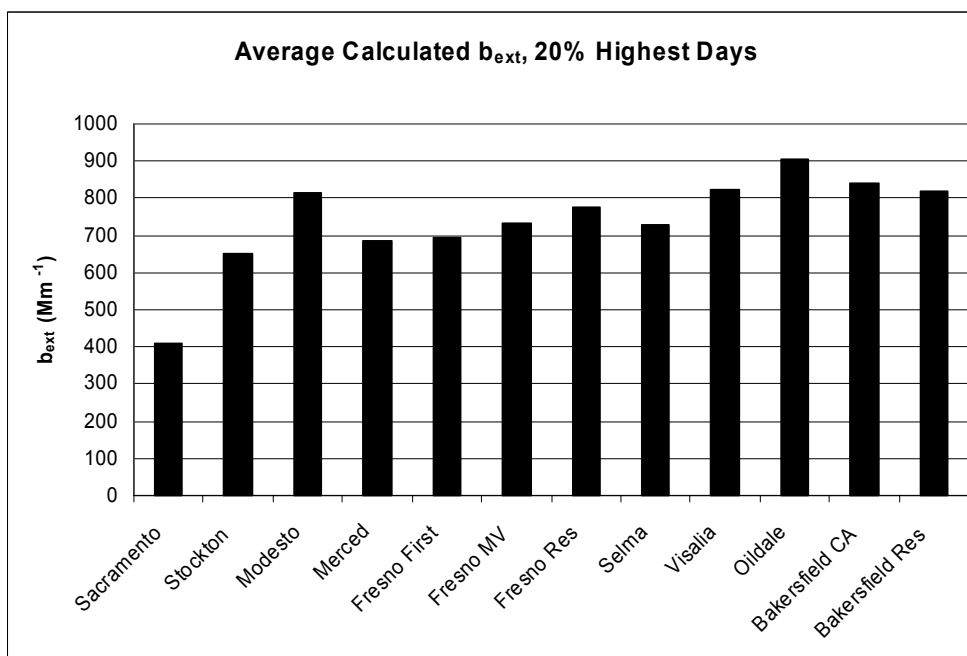


### 3.2 Where, How Much and How Often Do Individual Constituents Contribute to the Light Extinction Coefficient?

Chemical constituent contributions to the light extinction coefficient were evaluated separately for days with high, low and intermediate 24-hour average light extinction. High and low light extinction days were defined as the days with the 20 percent highest and 20 percent lowest calculated light extinction coefficient at each site. Intermediate light extinction days were defined as the other 60 percent of the days. The average light extinction coefficient and chemical constituent contributions were calculated for the days in each of these categories to assess where and how much individual constituents contributed to the light extinction coefficient. Additionally, the frequency with which the chemical constituents contributed various percentages of the daily calculated light extinction coefficient was examined to address how often the constituents contribute to the light extinction coefficient. The association between the calculated light extinction coefficient and exceedances of the 24-hour average PM<sub>2.5</sub> National Ambient Air Quality Standard (NAAQS) was also evaluated for the days with the 20 percent highest calculated light extinction coefficient.

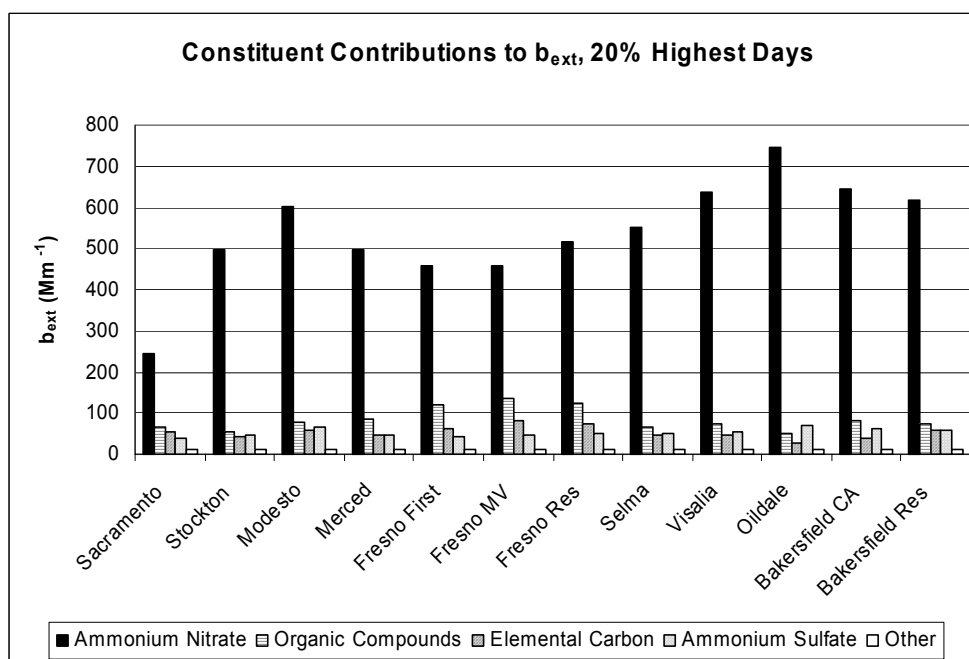
#### 3.2.1 Constituent Contributions During the 20 Percent Highest Days

Average calculated light extinction coefficients during the 20 percent highest days at each site are shown in Figure 3-2. The averages ranged from a little over 400 Mm<sup>-1</sup> at Sacramento, which was substantially lower than the other sites, to about 900 Mm<sup>-1</sup> at Oildale.



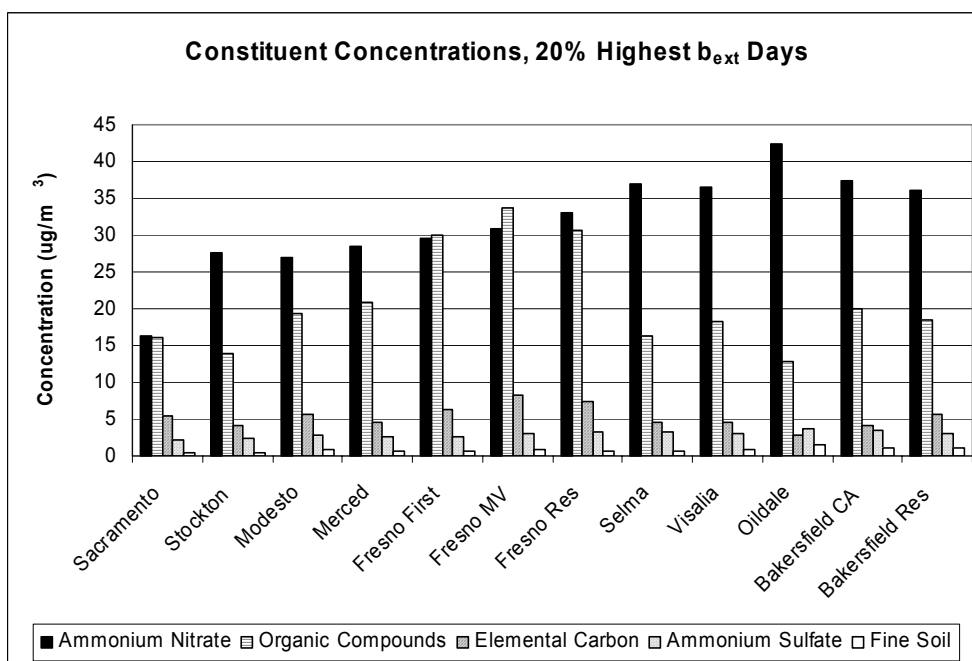
**Figure 3-2. Average Light Extinction Coefficient for the 20 Percent Highest Light Extinction Days by Site**

Average chemical constituent contributions to the light extinction coefficient during the days with the 20 percent highest total light extinction coefficient at each site are shown in Figure 3-3. The bar labeled “other” includes fine soil and light scattering by air molecules. Ammonium nitrate was the largest contributor at all sites, contributing from about 240  $\text{Mm}^{-1}$  at Sacramento to about 740  $\text{Mm}^{-1}$  at Oildale. The contribution from organic compounds was higher at the three Fresno sites than at the other sites.

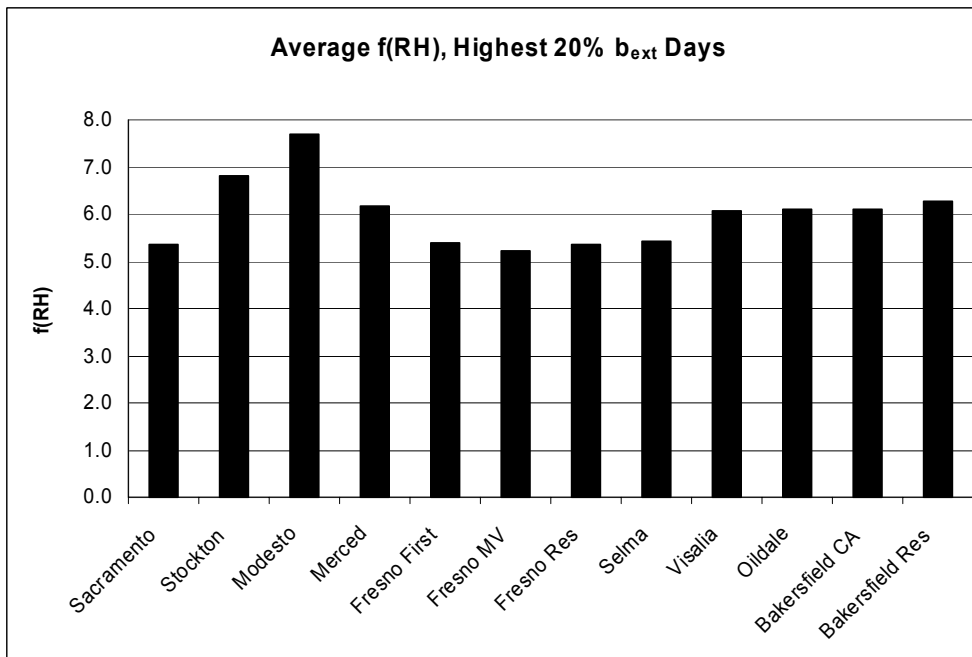


**Figure 3-3. Average Contributions of Chemical Constituents to 24-Hour Average Light Extinction Coefficient for the 20 Percent Highest Light Extinction Days by Site**

Figures 3-4 and 3-5 show the average chemical constituent concentrations and the average adjusted  $f(\text{RH})$  by site, respectively, for the 20 percent highest light extinction days. Comparing these figures with the ammonium nitrate contributions to the light extinction coefficient in Figure 3-3 indicates that variations in the contribution among sites was caused by differences in both ammonium nitrate concentration and in relative humidity. For example, Figures 3-4 and 3-5 show that the ammonium nitrate concentration was lower at Modesto than at Stockton and the three Fresno sites, but  $f(\text{RH})$  was higher. This higher  $f(\text{RH})$  led to a higher ammonium nitrate contribution to the light extinction coefficient at Modesto, as shown in Figure 3-3. On the other hand,  $f(\text{RH})$  was lower at Oildale than at several other sites, but the ammonium nitrate concentration was higher than at any other site, which led to the highest ammonium nitrate contribution to the light extinction coefficient.



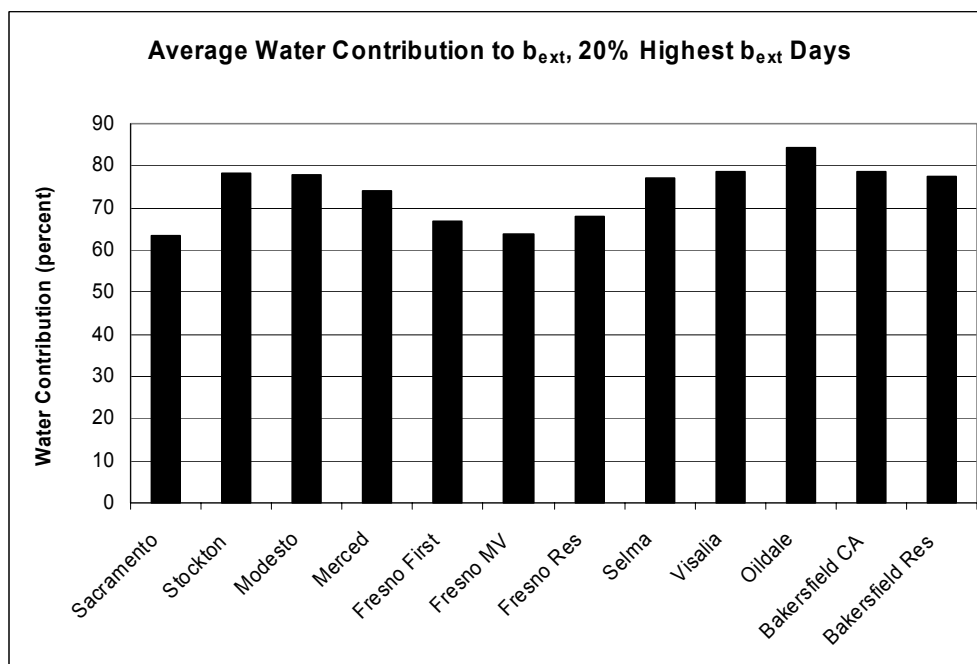
**Figure 3-4. Average Chemical Constituent Concentrations for the 20 Percent Highest Light Extinction Days by Site**



**Figure 3-5. Average  $f(RH)$  for the 20 Percent Highest Light Extinction Days by Site**

The average percentage of the calculated light extinction coefficient caused by water during the 20 percent highest light extinction days is shown by site in Figure 3-6. As seen in the figure, water

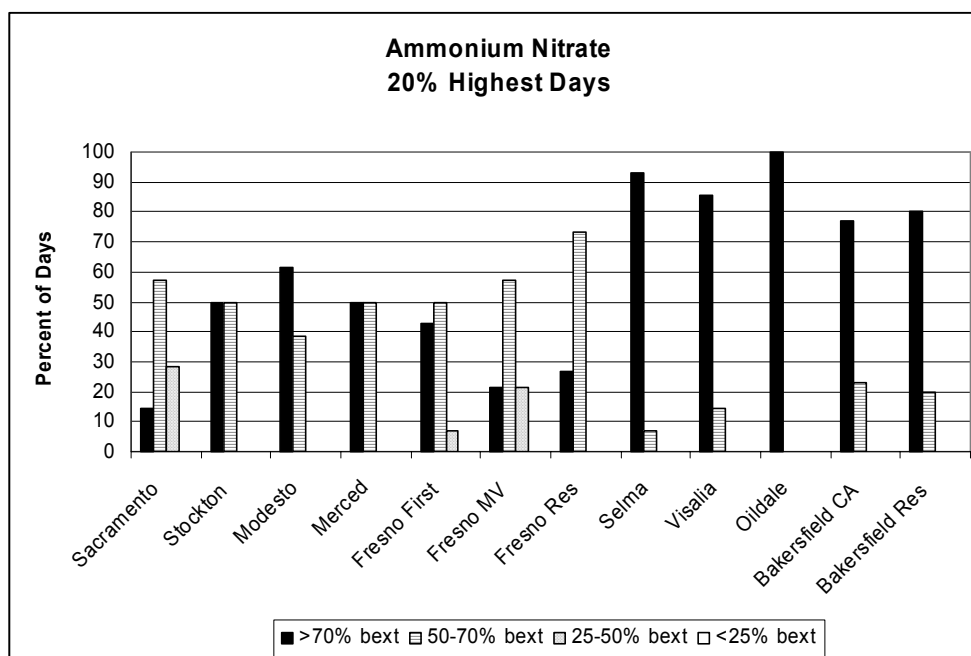
contributed more than 60 percent of the calculated light extinction coefficient at every site and more than 80 percent at Oildale. The percentage was lower at Sacramento and the three Fresno sites than at the other sites. This lower contribution was caused primarily by the lower average  $f(RH)$  at these sites, as seen in Figure 3-5.



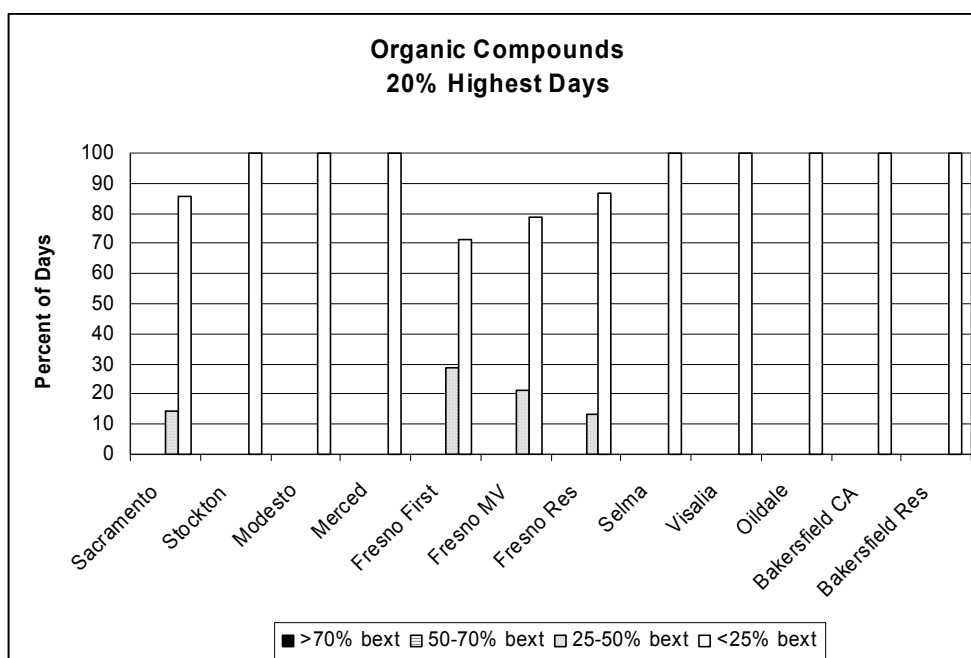
**Figure 3-6. Average Water Percentage Contribution to the Light Extinction Coefficient for the 20 Percent Highest Light Extinction Days by Site**

The frequency of ammonium nitrate, organic compound, elemental carbon and ammonium sulfate contributions to the light extinction coefficient during the 20 percent highest light extinction days are shown in Figures 3-7 through 3-10. These figures show the percentage of the 20 percent highest light extinction days at each site that each chemical constituent contributed 70 percent or more, 50 to 70 percent, 25 to 50 percent and less than 25 percent of the 24-hour average light extinction coefficient.

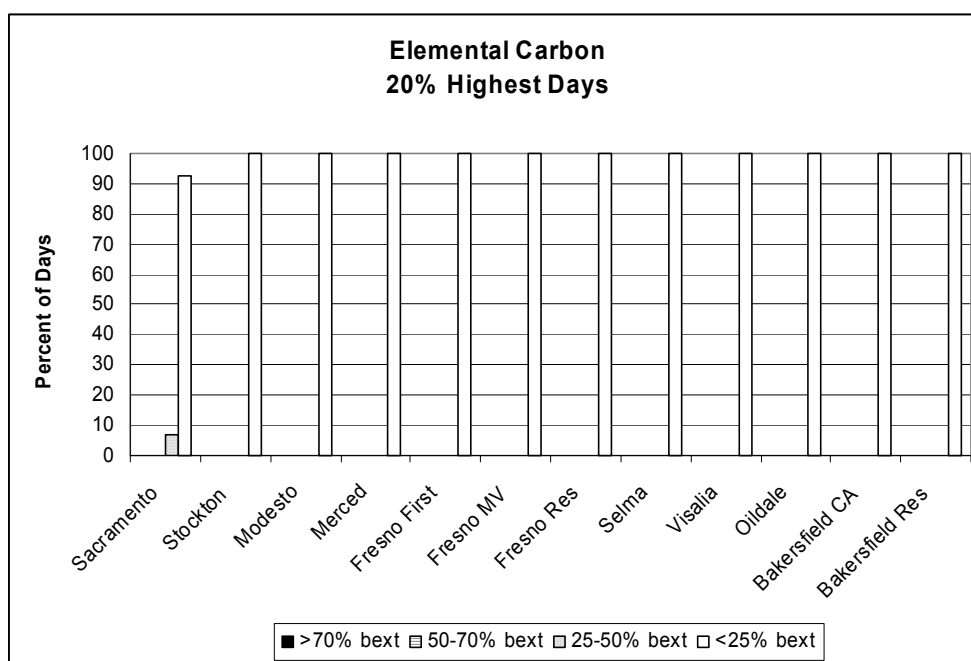
As seen in Figure 3-7, ammonium nitrate contributed 70 percent or more of the light extinction coefficient during most days at all of the sites except Sacramento and the three Fresno sites. It contributed 50 percent or more of the light extinction coefficient every day at all of the sites except Sacramento, where it contributed at least 50 percent of the light extinction coefficient on 70 percent of the days. Thus, ammonium nitrate was almost always the largest contributor, and frequently the dominant contributor, to the light extinction coefficient during the 20 percent highest days at all sites.



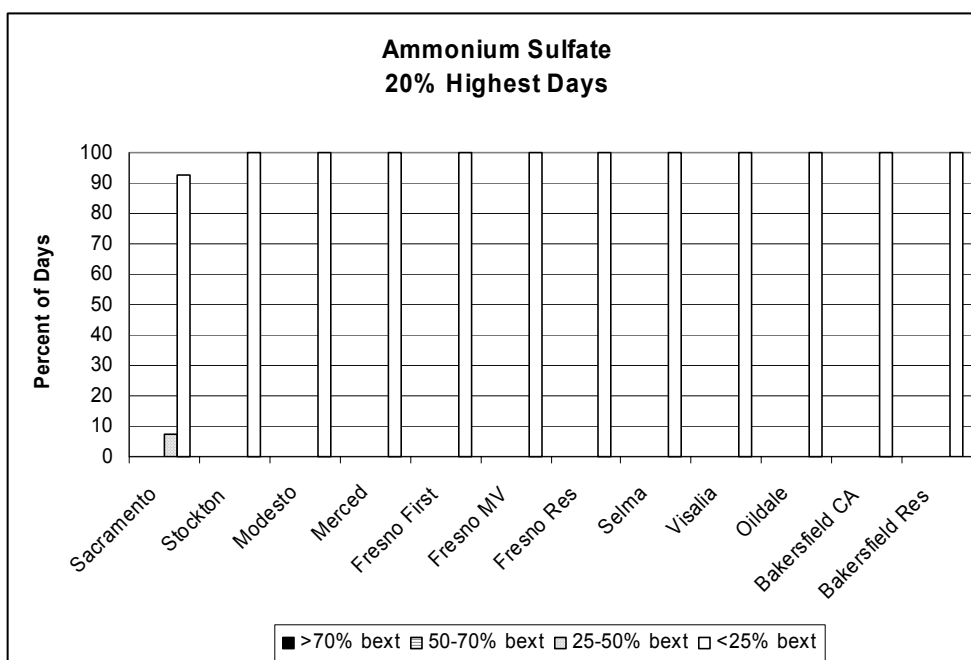
**Figure 3-7. Frequency of Ammonium Nitrate Contributions to the Light Extinction Coefficient On the 20 Percent Highest Light Extinction Days**



**Figure 3-8. Frequency of Organic Compounds Contributions to the Light Extinction Coefficient On the 20 Percent Highest Light Extinction Days**



**Figure 3-9. Frequency of Elemental Carbon Contributions to the Light Extinction Coefficient On the 20 Percent Highest Light Extinction Days**



**Figure 3-10. Frequency of Ammonium Sulfate Contributions to the Light Extinction Coefficient On the 20 Percent Highest Light Extinction Days**

Organic compounds only contributed more than 25 percent of the light extinction coefficient during a few days at Sacramento and the three Fresno sites (Figure 3-8). Elemental carbon (Figure 3-9) and ammonium sulfate (Figure 3-10) only accounted for more than 25 percent of the light extinction coefficient during one day each at Sacramento.

The previous results have indicated the importance of relative humidity as well as the concentrations of individual chemical constituents to causing high values of the light extinction coefficient. Associations between high values of the light extinction coefficient and exceedances of the 24-hour  $PM_{2.5}$  NAAQS were also examined. The purpose of this examination was to evaluate whether or not elevated values of the light extinction coefficient were always associated with  $PM_{2.5}$  mass concentrations that exceeded the NAAQS of  $65 \mu g/m^3$ .

The number of days and the average calculated light extinction coefficient for days when the measured  $PM_{2.5}$  mass concentration was greater than or less than or equal to the NAAQS on the days with the 20 percent highest light extinction coefficient at each site are listed in Table 3-2. The measured  $PM_{2.5}$  mass concentration was above the NAAQS on less than half of the days with the 20 percent highest light extinction coefficient at the northern sites (Sacramento, Stockton, Modesto and Merced), while it was above the NAAQS on more than half the days at the southern sites (the three Fresno sites, Selma, Visalia, Oildale and the two Bakersfield sites). The average calculated light extinction coefficient was 1.9 to 2.5 times higher at the northern sites when the NAAQS was exceed on the 20 percent highest light extinction coefficient days than when it was not. At most of the more southern sites, the calculated light extinction coefficient was less than twice as high when the NAAQS was exceeded on the 20 percent highest days than when it was not. Thus,  $PM_{2.5}$  concentrations were below the NAAQS on some days with poor visibility at all of the sites, but the frequency of days with poor visibility and  $PM_{2.5}$  concentrations below the NAAQS varied by site.

**Table 3-2**  
**Number of Days and Average Calculated  $b_{ext}$  on the 20 Percent Highest  $b_{ext}$  Days for Days with PM<sub>2.5</sub> Mass Above and Below the 24-Hour NAAQS**

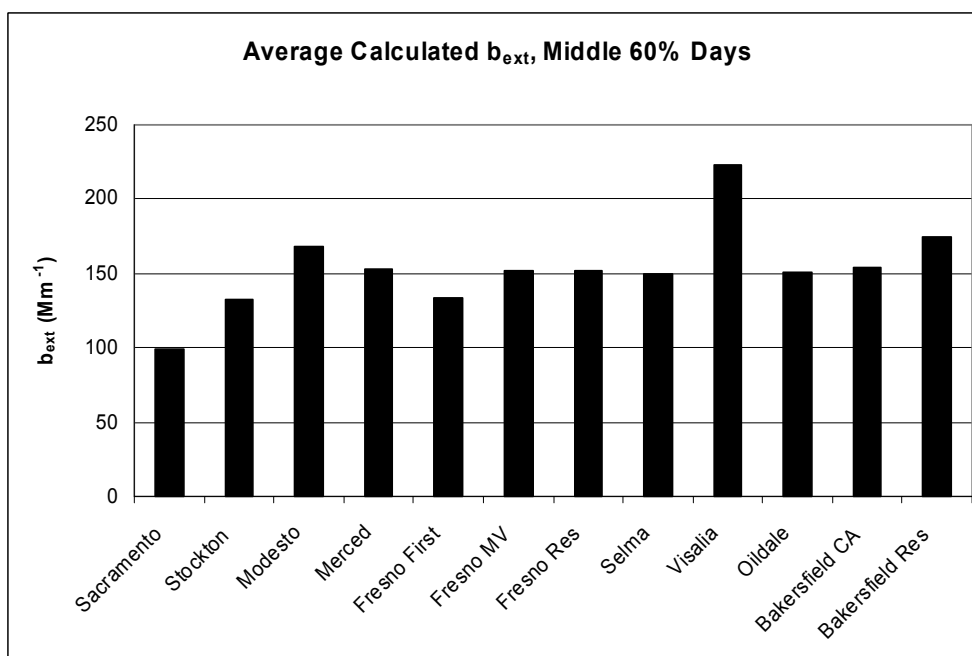
Site	Total Days <sup>a</sup>	PM <sub>2.5</sub> > NAAQS <sup>b</sup>		PM <sub>2.5</sub> ≤ NAAQS <sup>b</sup>		Average $b_{ext}$ > NAAQS/ Average $b_{ext}$ ≤ NAAQS
		No. Days	Average $b_{ext}$ (Mm <sup>-1</sup> )	No. Days	Average $b_{ext}$ (Mm <sup>-1</sup> )	
Sacramento	14	3	766	11	312	2.5
Stockton	11	3	1108	8	485	2.3
Modesto	13	5	1199	8	571	2.1
Merced	14	4	1030	10	545	1.9
Fresno First Street	14	9	781	5	542	1.4
Fresno Motor Vehicle	14	10	869	4	393	2.2
Fresno Residential	13	11	778	2	610	1.3
Selma	14	7	909	7	545	1.7
Visalia	13	9	946	4	562	1.7
Oildale	13	8	1116	5	570	2.0
Bakersfield California Ave.	13	8	1014	5	559	1.8
Bakersfield Residential	10	6	888	4	716	1.2
<sup>a</sup> Days with measured PM <sub>2.5</sub> mass concentrations and calculated light extinction coefficient <sup>b</sup> 24-Hour PM <sub>2.5</sub> National Ambient Air Quality Standard (NAAQS) is 65 µg/m <sup>3</sup>						

### 3.2.2 Constituent Contributions During the Middle 60 Percent Days

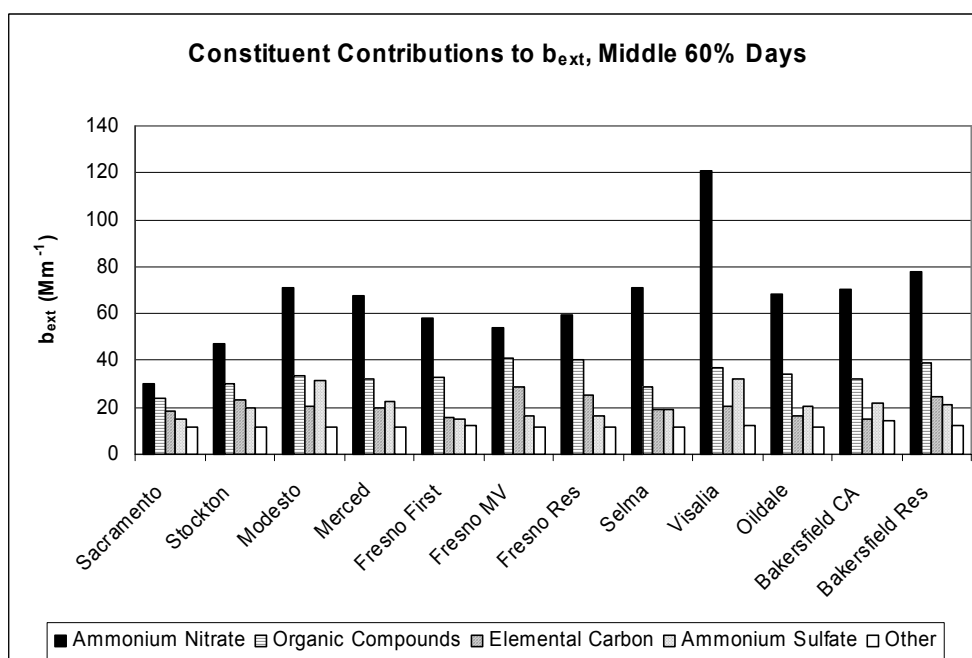
Average calculated light extinction coefficients during the middle 60 percent days at each site are shown in Figure 3-11. The averages ranged from about 100 Mm<sup>-1</sup> at Sacramento to about 225 Mm<sup>-1</sup> at Visalia.

Average chemical constituent contributions to the calculated light extinction coefficient during the middle 60 percent light extinction days are shown by site in Figure 3-12. Ammonium nitrate was the largest contributor on average during these days, but organic compounds accounted for more of the calculated light extinction than during the 20 percent highest light extinction days.



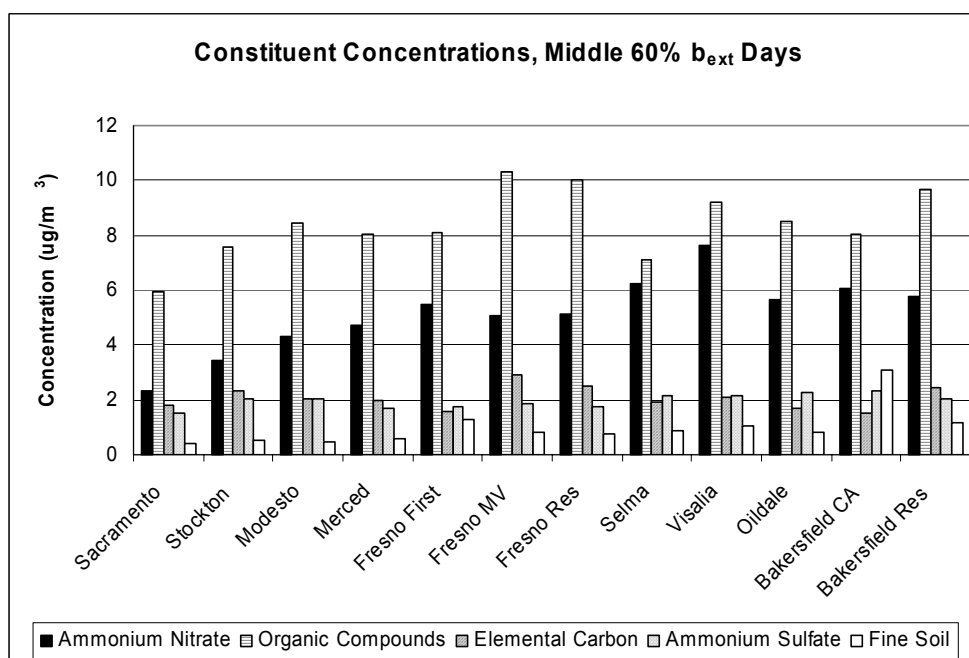


**Figure 3-11. Average Light Extinction Coefficient for the Middle 60 Percent Light Extinction Days by Site**

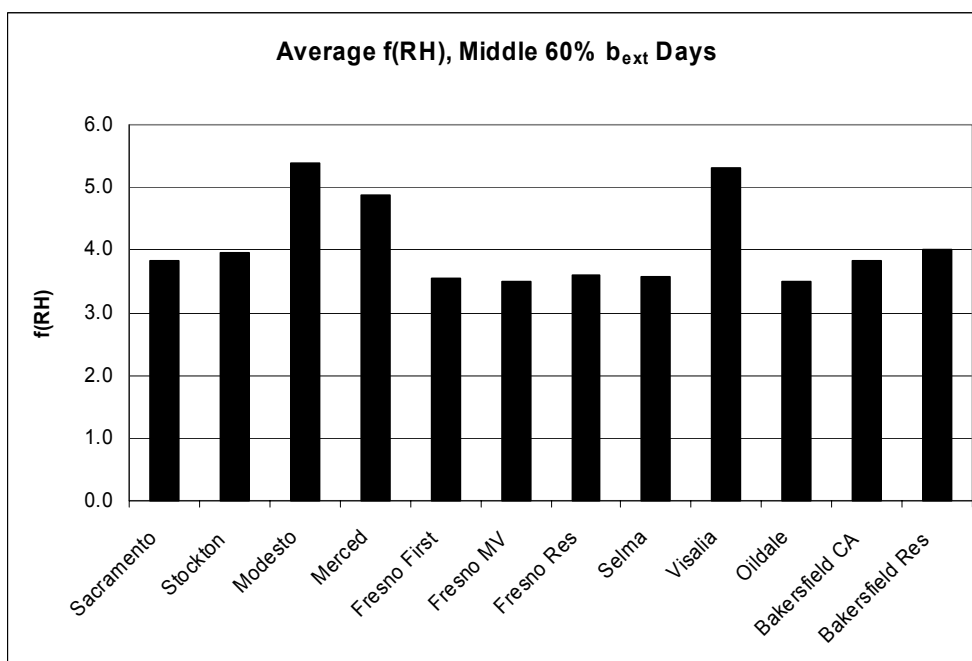


**Figure 3-12. Average Contributions of Chemical Constituents to 24-Hour Average Light Extinction Coefficient for the Middle 60% Light Extinction Days by Site**

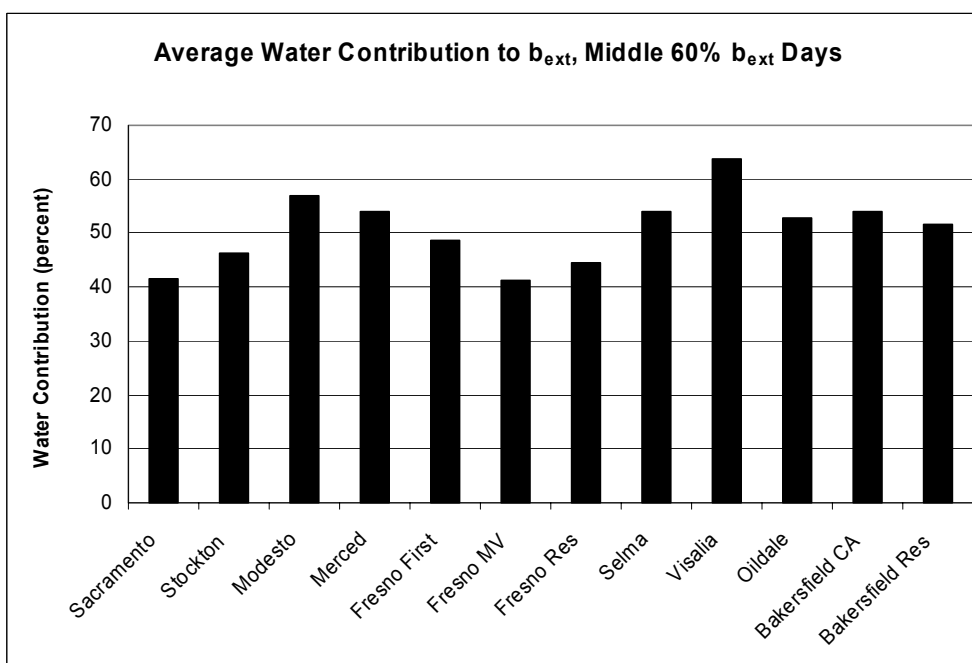
Average chemical constituent concentrations and adjusted  $f(RH)$  are shown by site for the middle 60 percent light extinction days in Figures 3-13 and 3-14. Although organic compound concentrations were higher than ammonium nitrate concentrations at all sites, as seen in Figure 3-13, water associated with ammonium nitrate caused the ammonium nitrate contribution to the light extinction coefficient to exceed the organic compound contribution. As seen in Figure 3-15, which shows the average percentage contribution of water to the calculated light extinction coefficient during the middle 60 percent days, water accounted for more than 40 percent of the calculated light extinction coefficient at all sites and over 60 percent of the light extinction coefficient at Visalia.



**Figure 3-13. Average Chemical Constituent Concentrations for the Middle 60 Percent Light Extinction Days by Site**



**Figure 3-14. Average f(RH) for the Middle 60 Percent Light Extinction Days by Site**

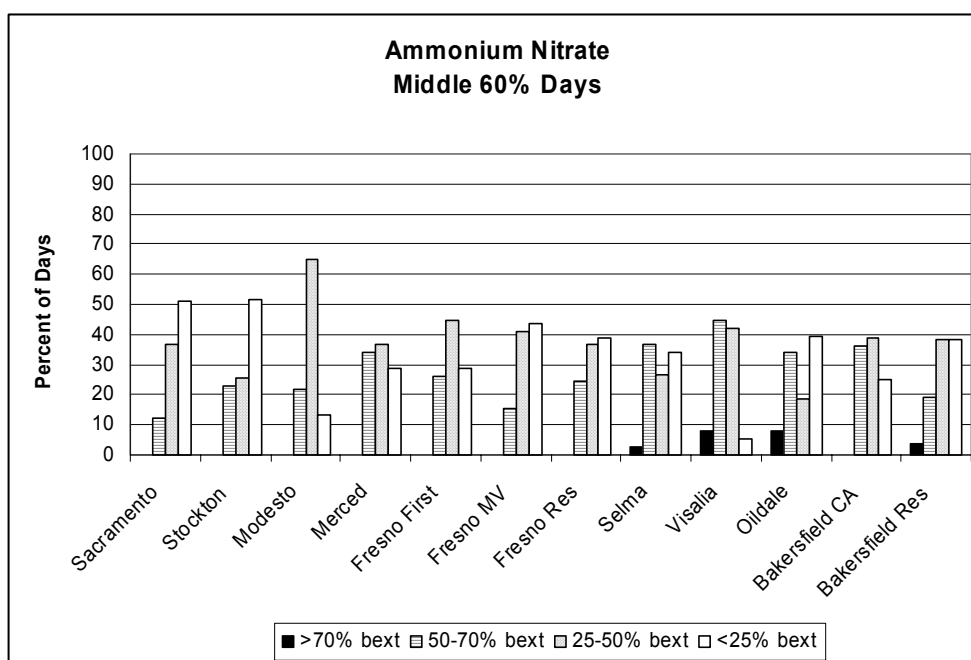


**Figure 3-15. Average Water Percentage Contribution to the Light Extinction Coefficient for the Middle 60 Percent Light Extinction Days by Site**

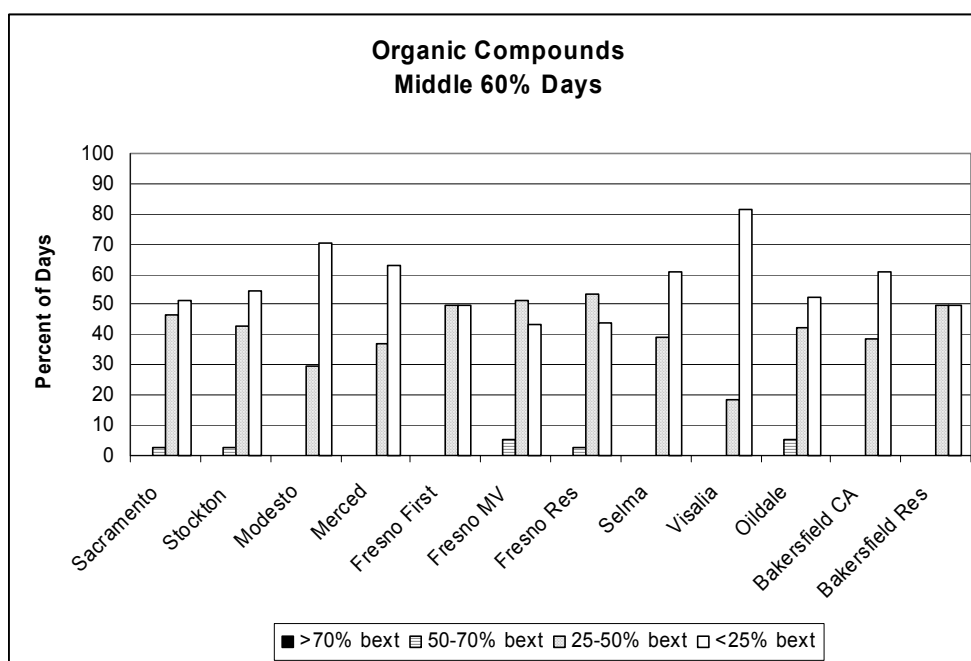
The frequency of ammonium nitrate, organic compound, elemental carbon and ammonium sulfate contributions to the light extinction coefficient during the middle 60 percent light extinction days

are shown in Figures 3-16 through 3-19. As seen in Figure 3-16, ammonium nitrate never contributed more than 70 percent of the light extinction coefficient at most of the sites, and only rarely contributed more than 70 percent at Selma, Visalia, Oildale and the Bakersfield Residential site. It accounted for 50 to 70 percent of the light extinction on fewer than 40 percent of the days at all sites except Visalia and accounted for less than 25 percent of the light extinction on more than half the days at Sacramento and Stockton. Thus, ammonium nitrate accounted for a large fraction of the light extinction coefficient less frequently during the middle 60 percent light extinction days than during the 20 percent highest days.

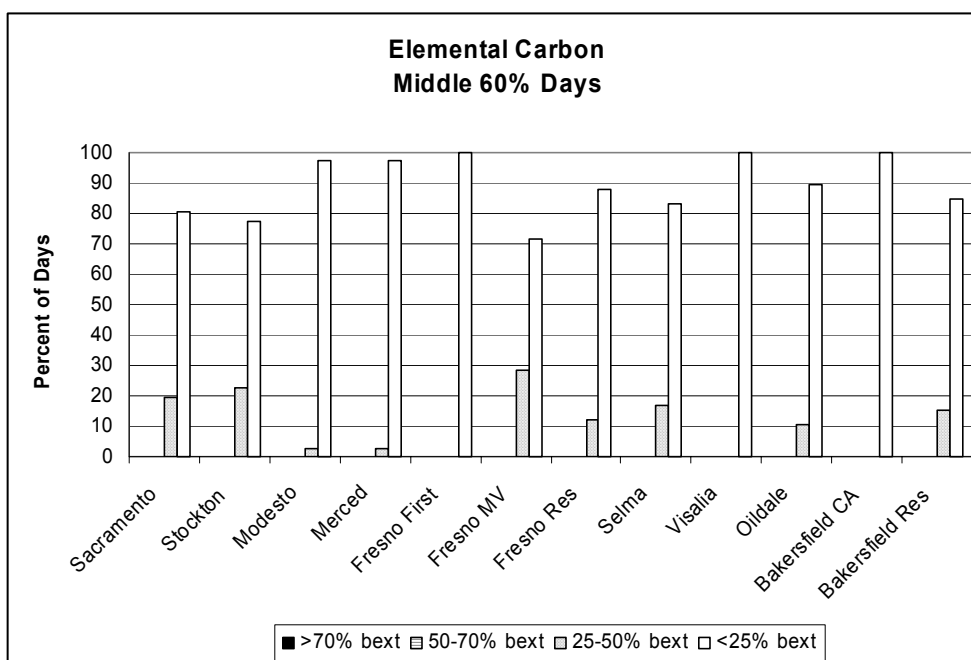
As seen in Figure 3-17, organic compounds accounted for more than 25 percent of the light extinction coefficient during 40 percent or more of the days at most of the sites and accounted for more than half the light extinction coefficient during one day each at Sacramento and the Fresno Residential sites and during two days at the Fresno Motor Vehicle site. Thus, organic compounds contributed a substantial fraction of the light extinction coefficient more frequently during the middle 60 percent light extinction days than during the 20 percent highest days.



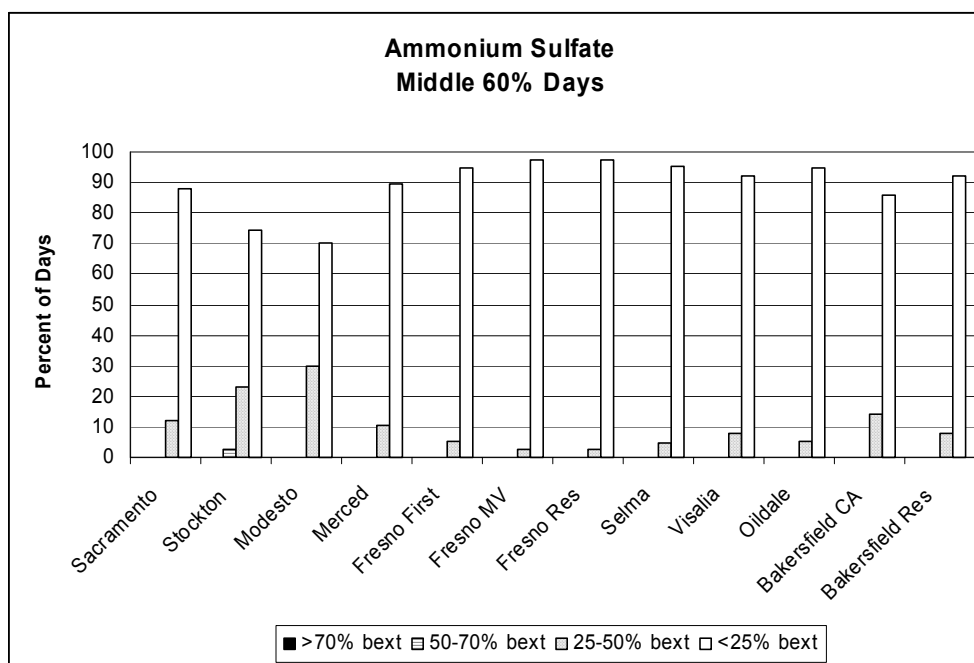
**Figure 3-16. Frequency of Ammonium Nitrate Contributions to the Light Extinction Coefficient On the Middle 60 Percent Light Extinction Days**



**Figure 3-17. Frequency of Organic Compounds Contributions to the Light Extinction Coefficient On the Middle 60 Percent Light Extinction Days**



**Figure 3-18. Frequency of Elemental Carbon Contributions to the Light Extinction Coefficient On the Middle 60 Percent Light Extinction Days**



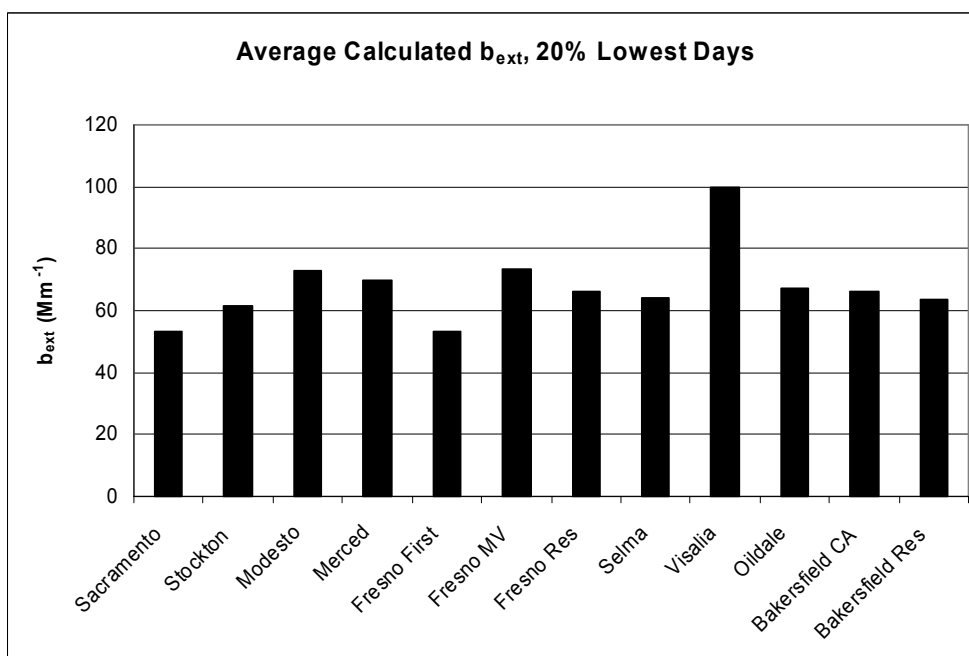
**Figure 3-19. Frequency of Ammonium Sulfate Contributions to the Light Extinction Coefficient On the Middle 60 Percent Light Extinction Days**

As seen in Figure 3-18, elemental carbon accounted for more than 25 percent of the light extinction on more than 10 percent of the days at seven of the 12 sites. Ammonium sulfate accounted for more than 50 percent of the light extinction coefficient one day at Stockton and more than 25 percent on more than 10 percent of the days at five sites.

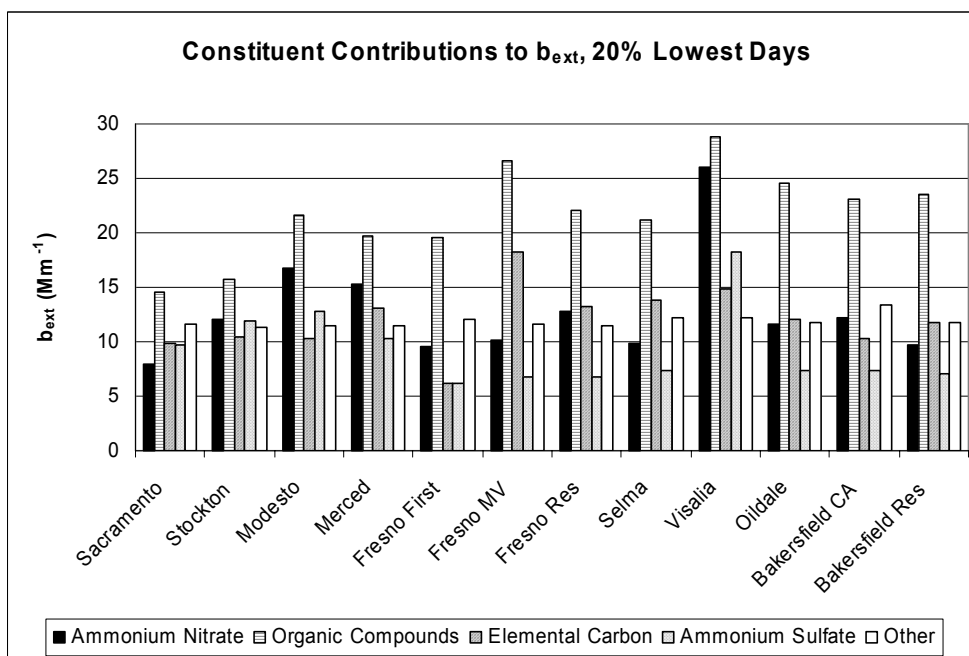
### 3.2.3 Constituent Contributions During the 20 Percent Lowest Days

Average calculated light extinction coefficients during the 20 percent lowest days at each site are shown in Figure 3-20. The averages ranged from about  $55 \text{ Mm}^{-1}$  at Sacramento and the Fresno First Street site to about  $100 \text{ Mm}^{-1}$  at Visalia.

Average chemical constituent contributions to the calculated light extinction coefficient during the 20 percent lowest light extinction days are shown by site in Figure 3-21. Organic compounds were the largest contributor at all sites, but ammonium nitrate was a major contributor at some sites, particularly Stockton, Modesto, Merced and Visalia. It should be noted, however, that sampling was conducted every six days at these sites, so the 20 percent lowest days include 14 or fewer days at each site. If more frequent sampling had been conducted, the 20 percent lowest days may have included more days during the summer with lower relative humidity and higher temperatures, which would probably have had lower ammonium nitrate concentrations and lower resulting contributions to the light extinction coefficient.



**Figure 3-20. Average Light Extinction Coefficient for the 20 Percent Lowest Light Extinction Days by Site**



**Figure 3-21. Average Contributions of Chemical Constituents to 24-Hour Average Light Extinction Coefficient for the 20 Percent Lowest Light Extinction Days by Site**

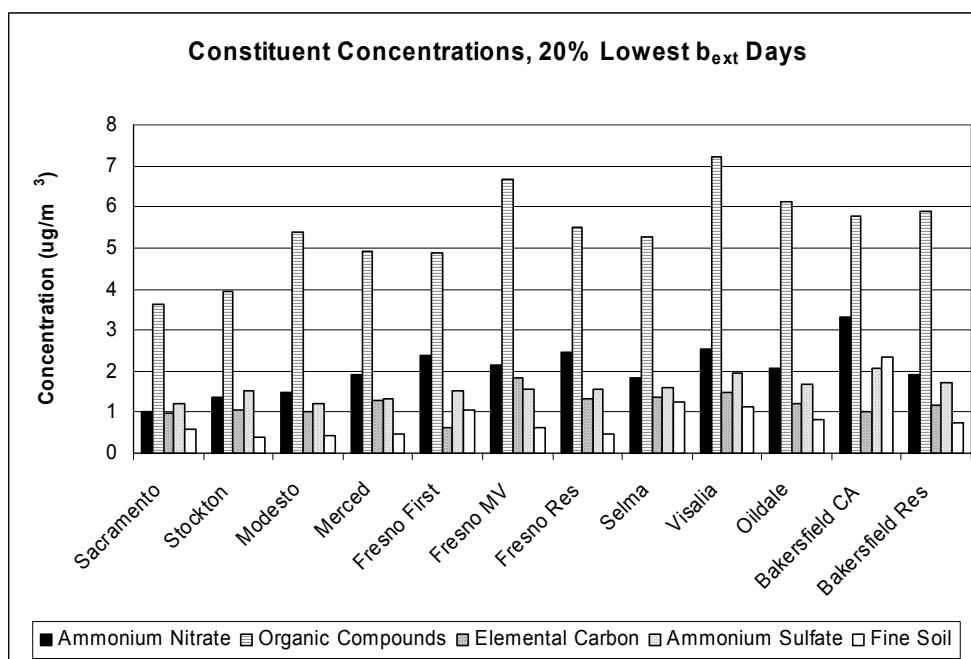
Average chemical constituent concentrations and adjusted  $f(RH)$  are shown by site for the 20 percent lowest light extinction days in Figures 3-22 and 3-23. Organic compound concentrations were higher than any other constituent at all sites. Average  $f(RH)$  was higher at Stockton, Modesto, Merced and Visalia, as seen in Figure 3-23, which led to the relatively high ammonium nitrate contribution to the light extinction coefficient at these sites. As seen in Figure 3-24, which shows the average percentage contribution of water to the calculated light extinction coefficient during the 20 percent lowest days, water accounted for less than 25 percent of the calculated light extinction coefficient at many sites and no more than 40 percent at any site.

The frequency of ammonium nitrate, organic compound, elemental carbon and ammonium sulfate contributions to the light extinction coefficient during the 20 percent lowest light extinction days are shown in Figures 3-25 through 3-28. As seen in Figure 3-25, ammonium nitrate contributed less than 25 percent of the light extinction coefficient during 70 percent or more of the days at all sites except Visalia, where it contributed more than 25 percent on 50 percent of the days. Thus, ammonium nitrate rarely accounted for a substantial fraction of the light extinction coefficient during the 20 percent lowest light extinction days.

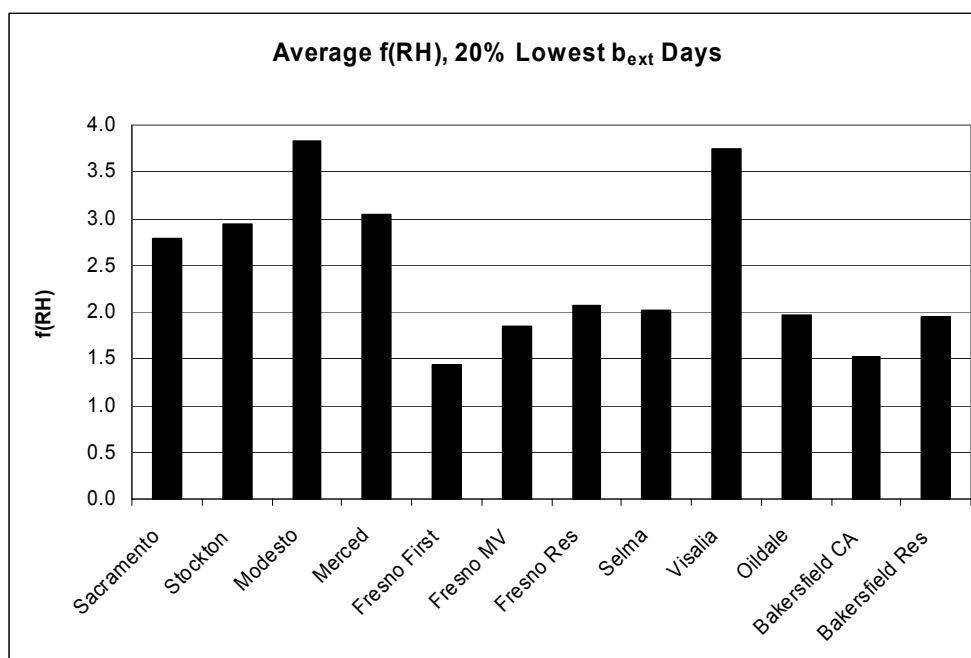
As seen in Figure 3-26, organic compounds accounted for more than 25 percent of the light extinction coefficient during 50 percent or more of the days at all of the sites except Sacramento and on 70 percent or more of the days at seven of the 12 sites. Thus, organic compounds frequently contributed a substantial fraction of the light extinction coefficient during the 20 percent lowest days.

As seen in Figure 3-27, elemental carbon occasionally accounted for more than 25 percent of the light extinction at several of the sites and accounted for more than 25 percent on more than 50 percent of the days at the Fresno Motor Vehicle site. Ammonium sulfate also occasionally accounted for more than 25 percent of the light extinction coefficient at some sites, but never accounted for more than 25 percent at six of the 12 sites.

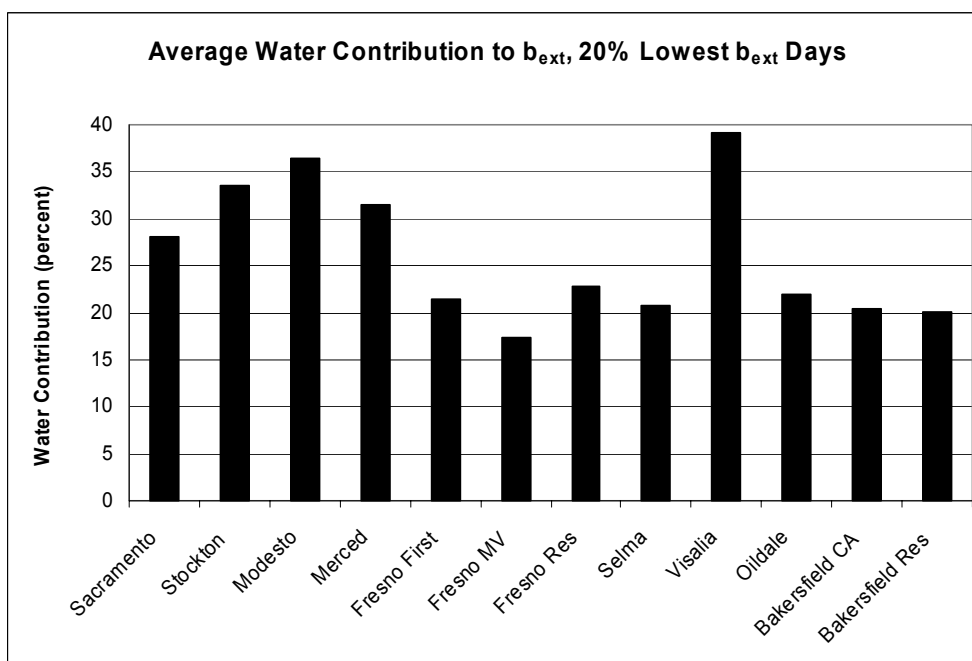




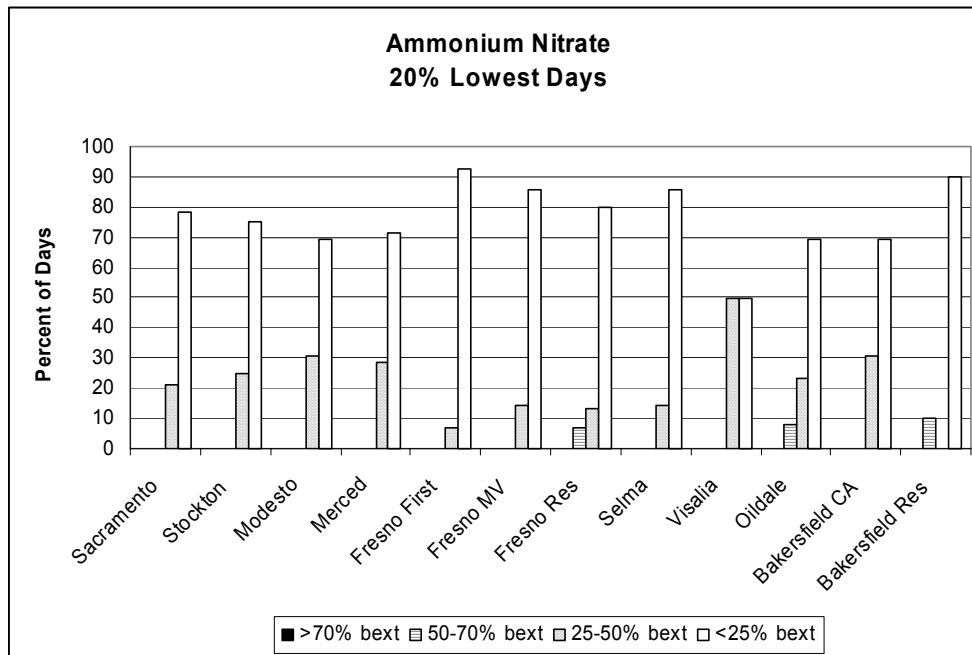
**Figure 3-22. Average Chemical Constituent Concentrations for the 20 Percent Lowest Light Extinction Days by Site**



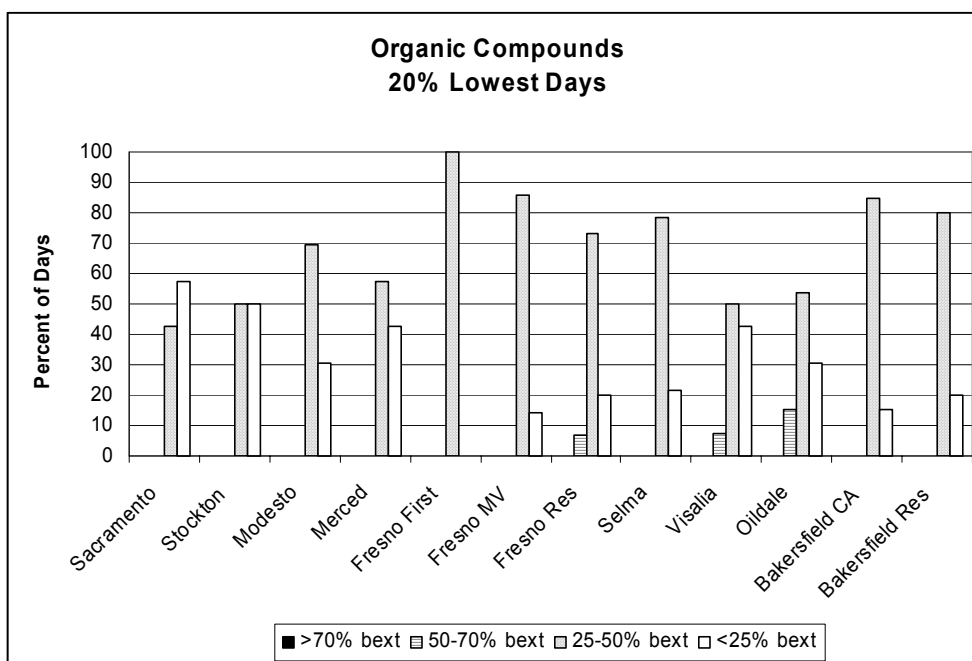
**Figure 3-23. Average  $f(RH)$  for the 20 Percent Lowest Light Extinction Days by Site**



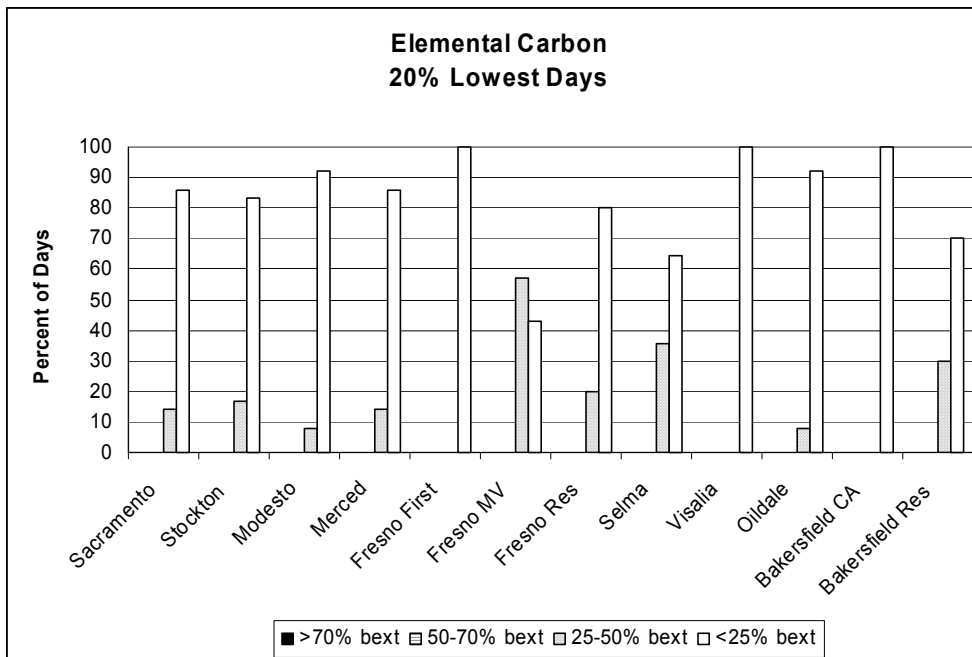
**Figure 3-24. Average Water Percentage Contribution to the Light Extinction Coefficient for the 20 Percent Lowest Light Extinction Days by Site**



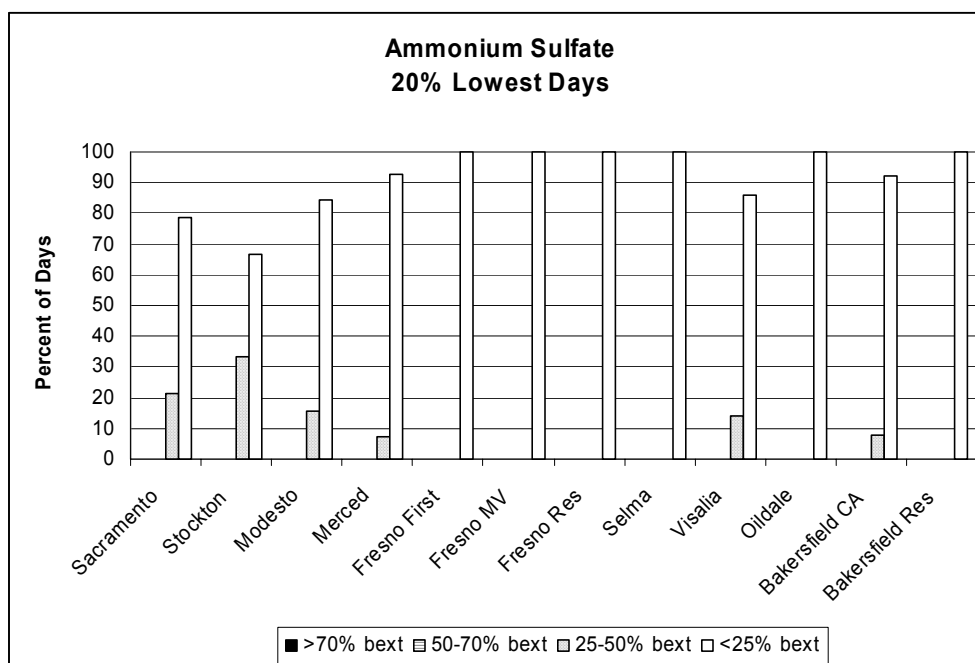
**Figure 3-25. Frequency of Ammonium Nitrate Contributions to the Light Extinction Coefficient On the 20 Percent Lowest Light Extinction Days**



**Figure 3-26. Frequency of Organic Compounds Contributions to the Light Extinction Coefficient On the 20 Percent Lowest Light Extinction Days**



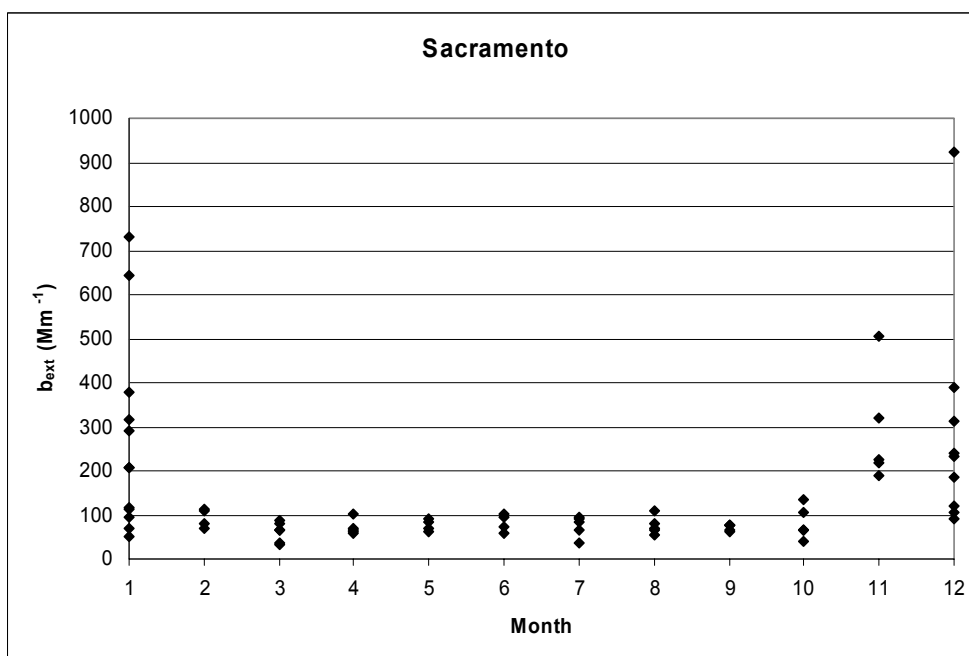
**Figure 3-27. Frequency of Elemental Carbon Contributions to the Light Extinction Coefficient On the 20 Percent Lowest Light Extinction Days**



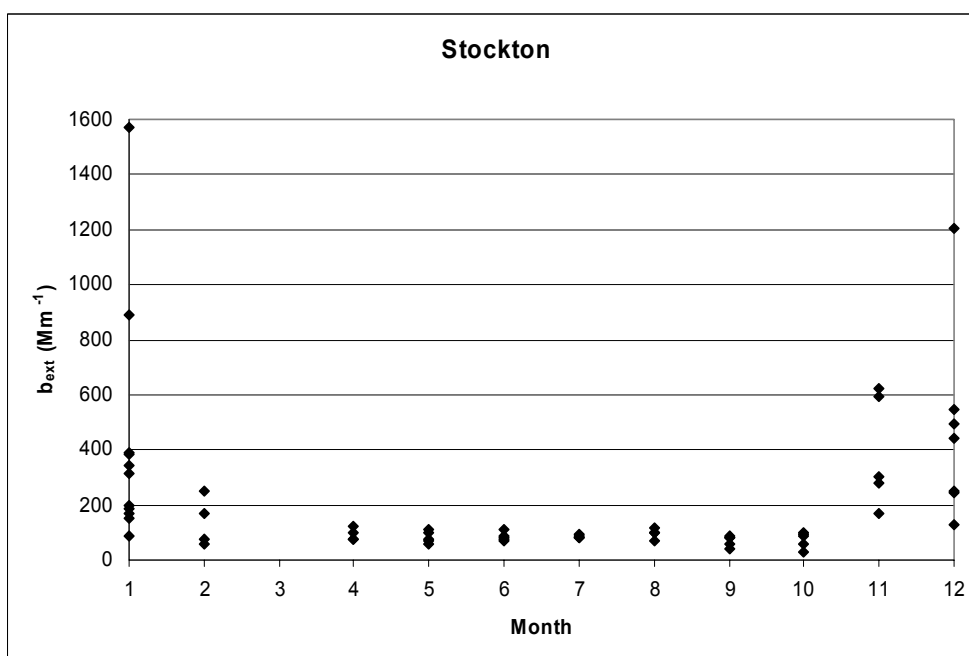
**Figure 3-28. Frequency of Ammonium Sulfate Contributions to the Light Extinction Coefficient On the 20 Percent Lowest Light Extinction Days**

### 3.3 How Does the Light Extinction Coefficient Vary During the Year?

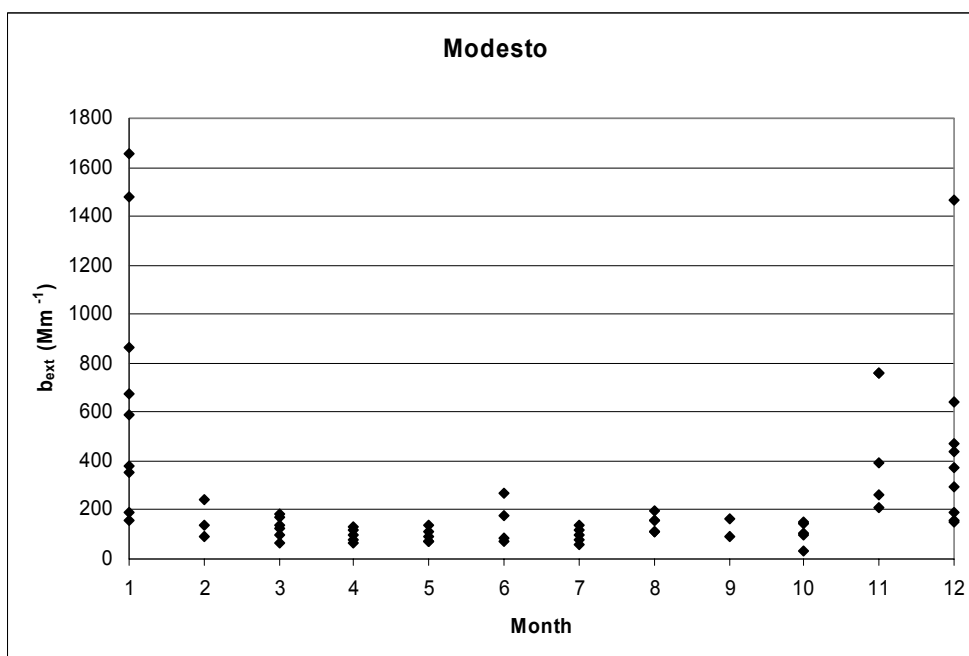
Monthly variations in the light extinction coefficient were characterized by plotting individual values of the 24-hour average calculated light extinction coefficient by month for each site, as shown in Figures 3-29 through 3-40. The highest values during the year occurred during January, November and December at all sites, although low values also occurred during these months. High values also occurred during October at the Fresno and Visalia sites. The calculated light extinction coefficient was generally low from April through September.



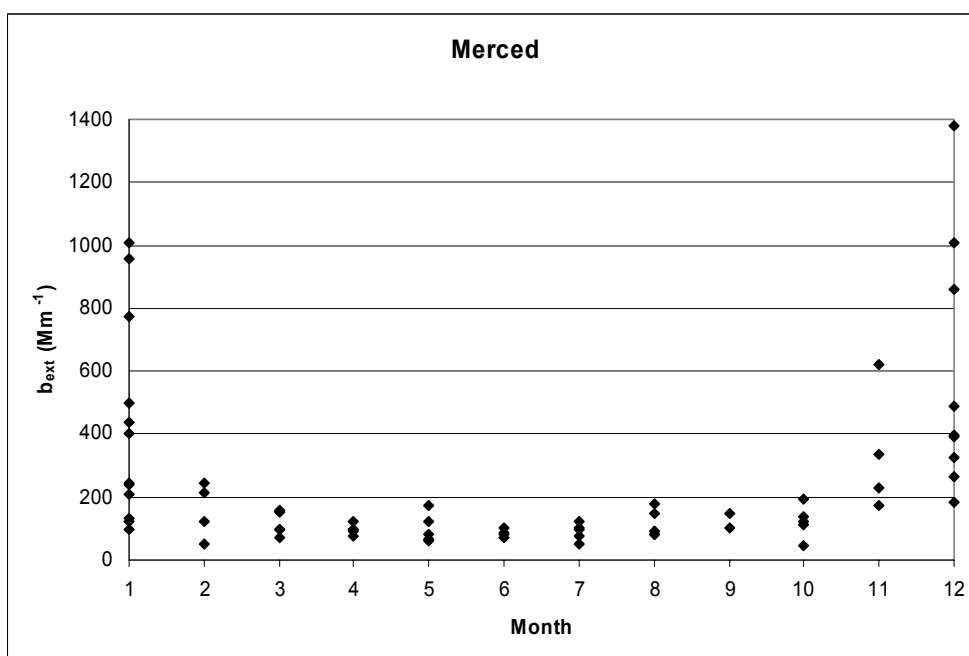
**Figure 3-29. Calculated Light Extinction Coefficient During Individual Days by Month for Sacramento**



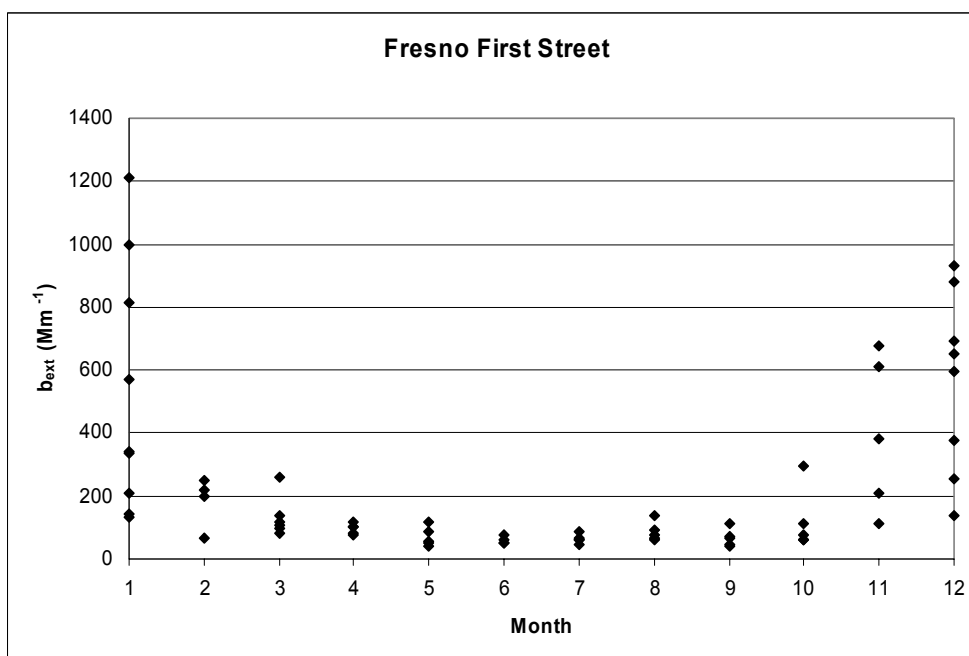
**Figure 3-30. Calculated Light Extinction Coefficient During Individual Days by Month for Stockton**



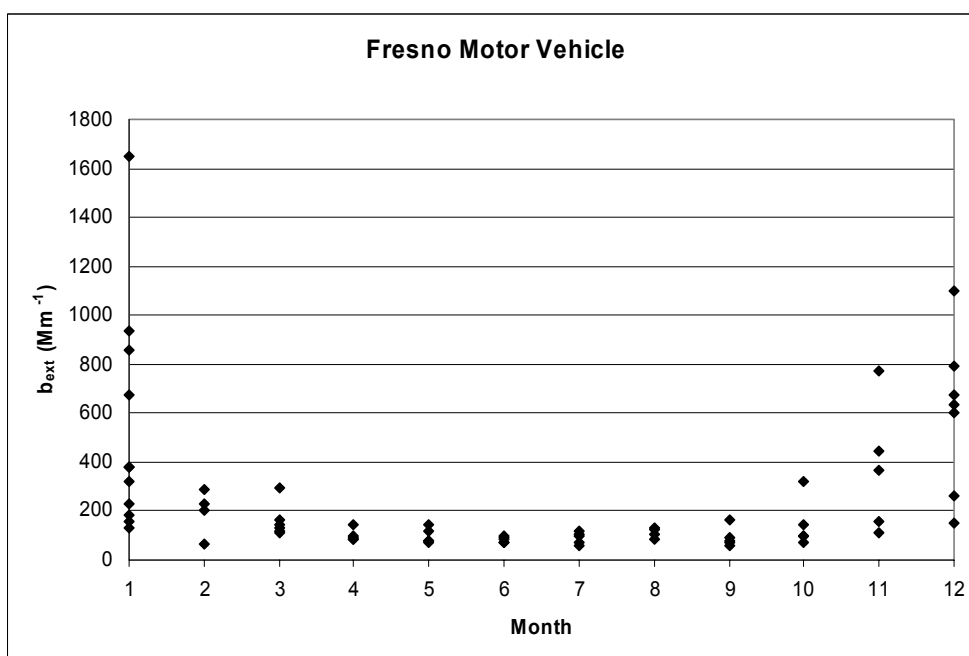
**Figure 3-31. Calculated Light Extinction Coefficient During Individual Days by Month for Modesto**



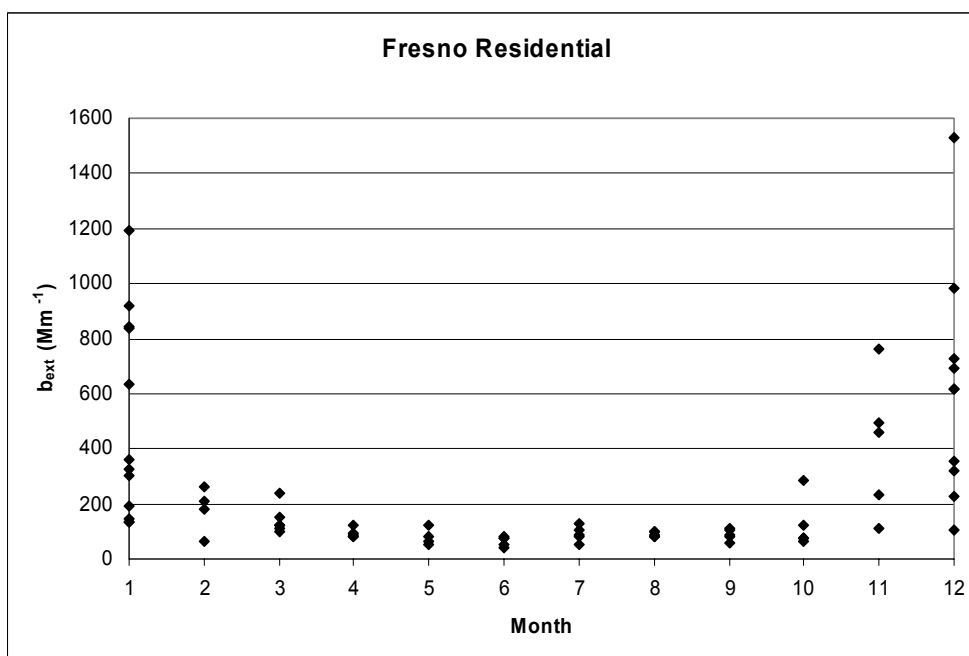
**Figure 3-32. Calculated Light Extinction Coefficient During Individual Days by Month for Merced**



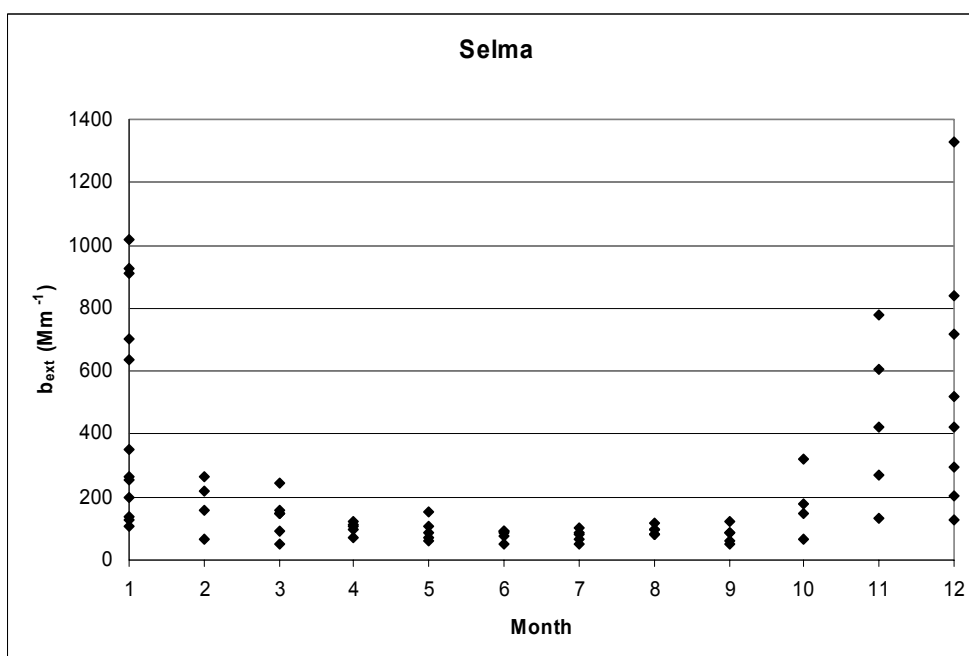
**Figure 3-33. Calculated Light Extinction Coefficient During Individual Days by Month for Fresno First Street**



**Figure 3-34. Calculated Light Extinction Coefficient During Individual Days by Month for Fresno Motor Vehicle**

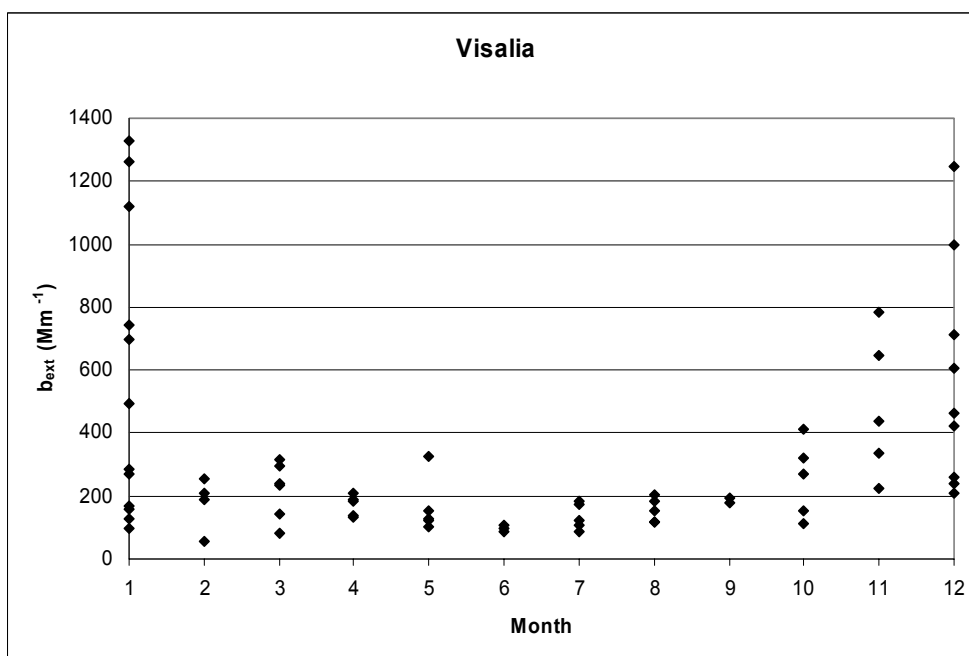


**Figure 3-35. Calculated Light Extinction Coefficient During Individual Days by Month for Fresno Residential**

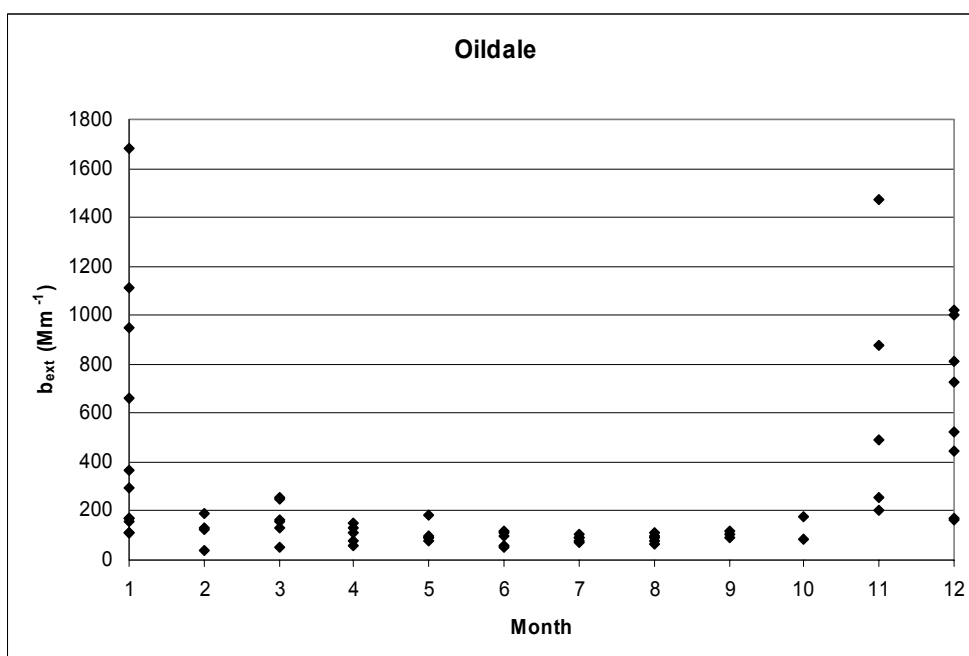


**Figure 3-36. Calculated Light Extinction Coefficient During Individual Days by Month for Selma**

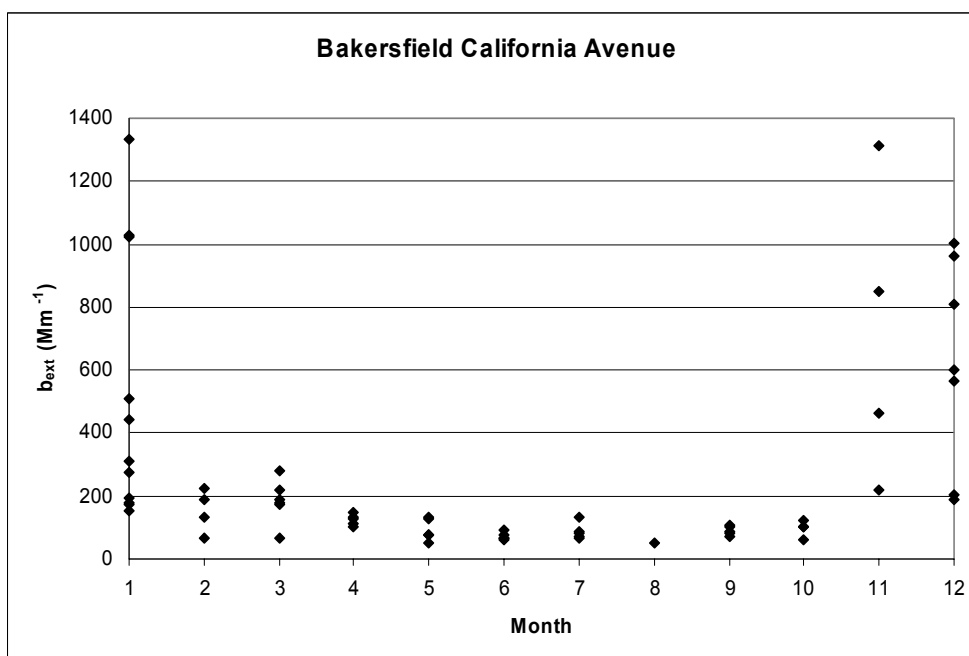




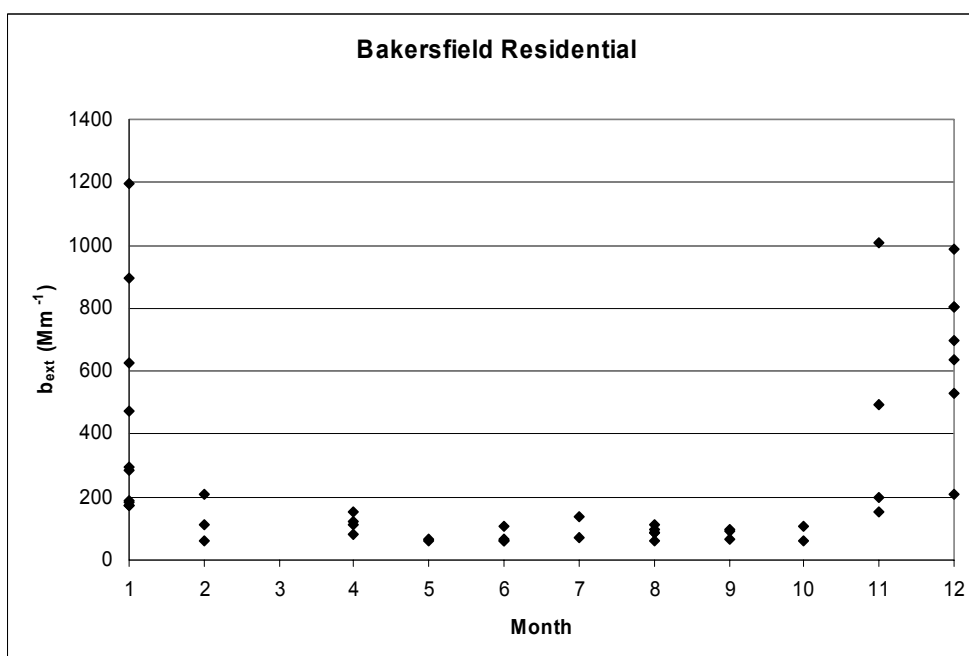
**Figure 3-37. Calculated Light Extinction Coefficient During Individual Days by Month for Visalia**



**Figure 3-38. Calculated Light Extinction Coefficient During Individual Days by Month for Oildale**



**Figure 3-39. Calculated Light Extinction Coefficient During Individual Days by Month for Bakersfield California Avenue**

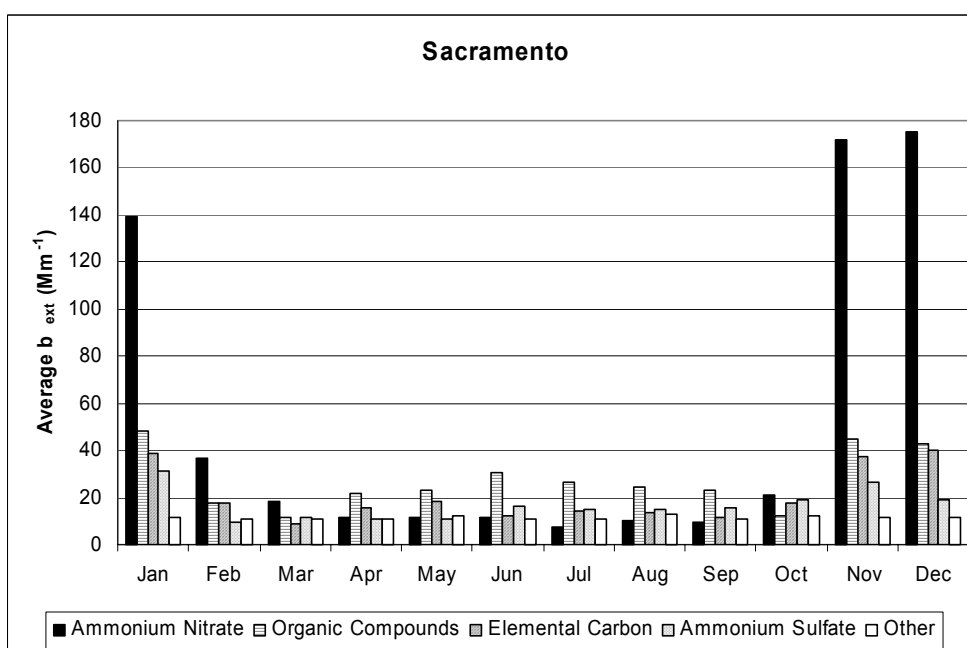


**Figure 3-40. Calculated Light Extinction Coefficient During Individual Days by Month for Bakersfield Residential**

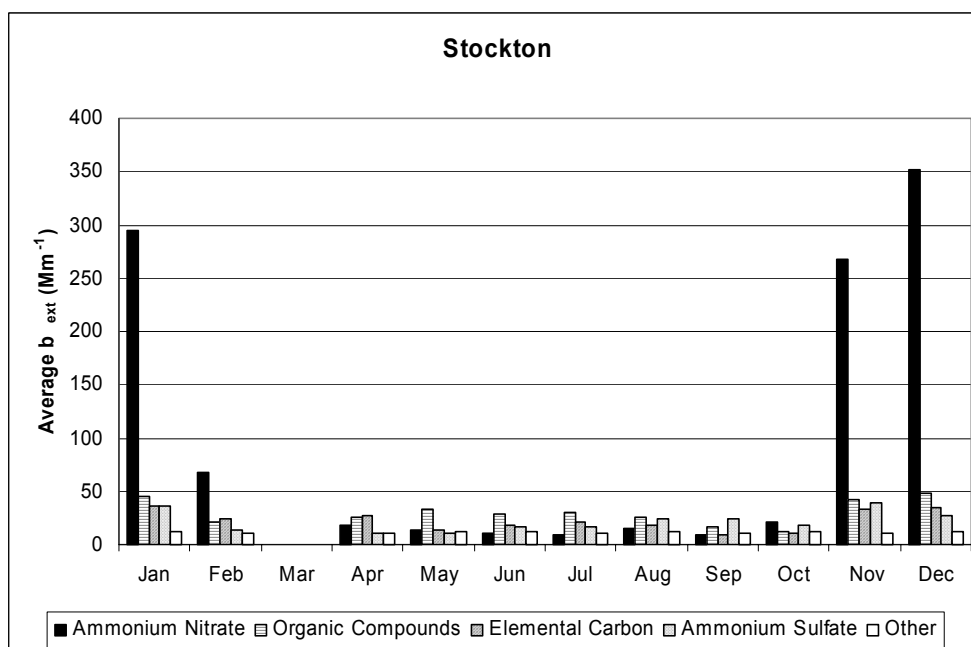
### 3.4 When During the Year Do Individual Constituents Contribute to the Light Extinction Coefficient?

Monthly average chemical constituent contributions to the light extinction coefficient are shown for each site in Figures 3-41 through 3-52. Average ammonium nitrate contributions were higher during January, February, November and December than during other months at all sites. The highest average contributions from organic compounds also occurred during January, November and December, particularly at Sacramento and the Fresno sites, which are located in more populated urban areas than the other sites.

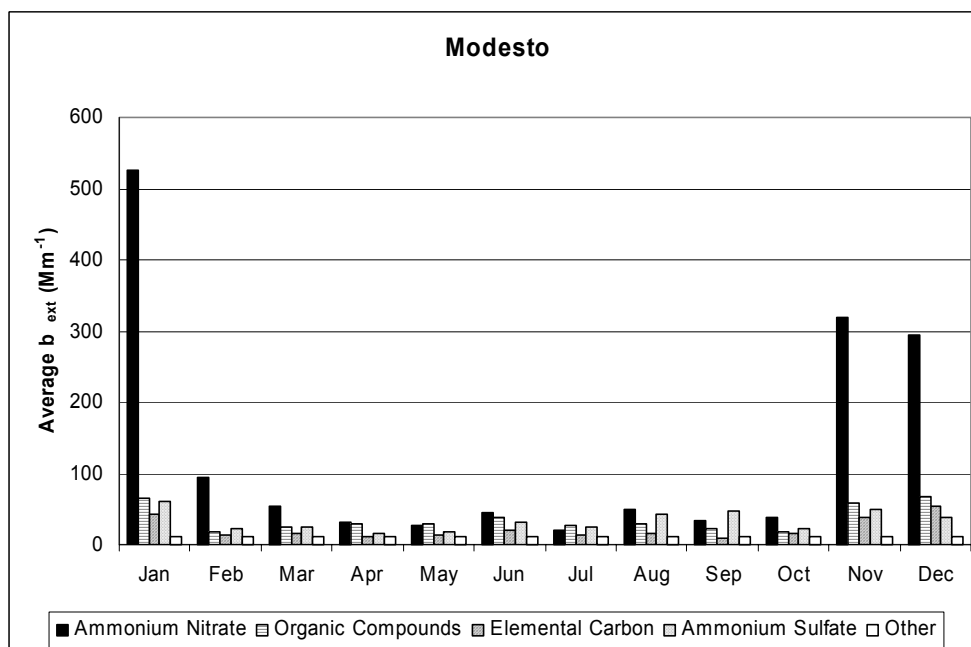
Ammonium nitrate was the largest contributor to the light extinction coefficient during January, November and December at all sites as well as during March and October at some sites. Organic compounds were the largest contributor at most sites from April through September.



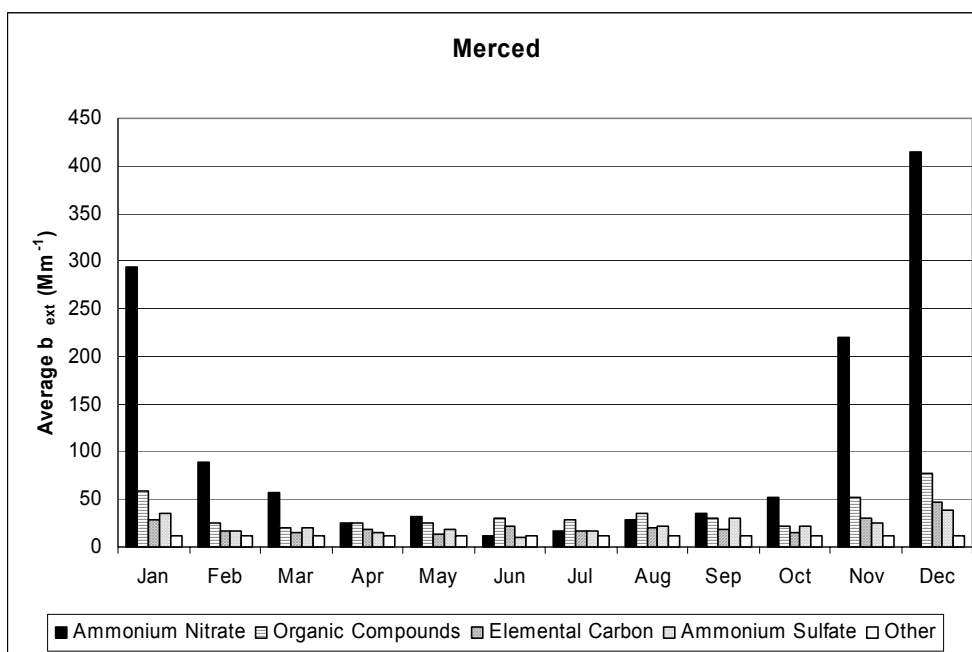
**Figure 3-41. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Sacramento**



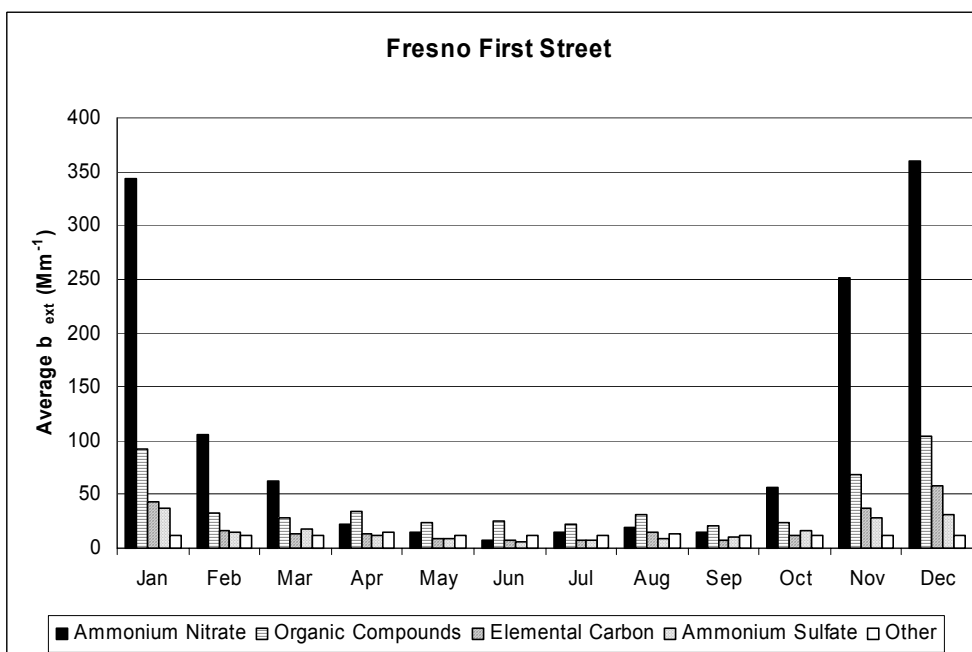
**Figure 3-42. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Stockton**



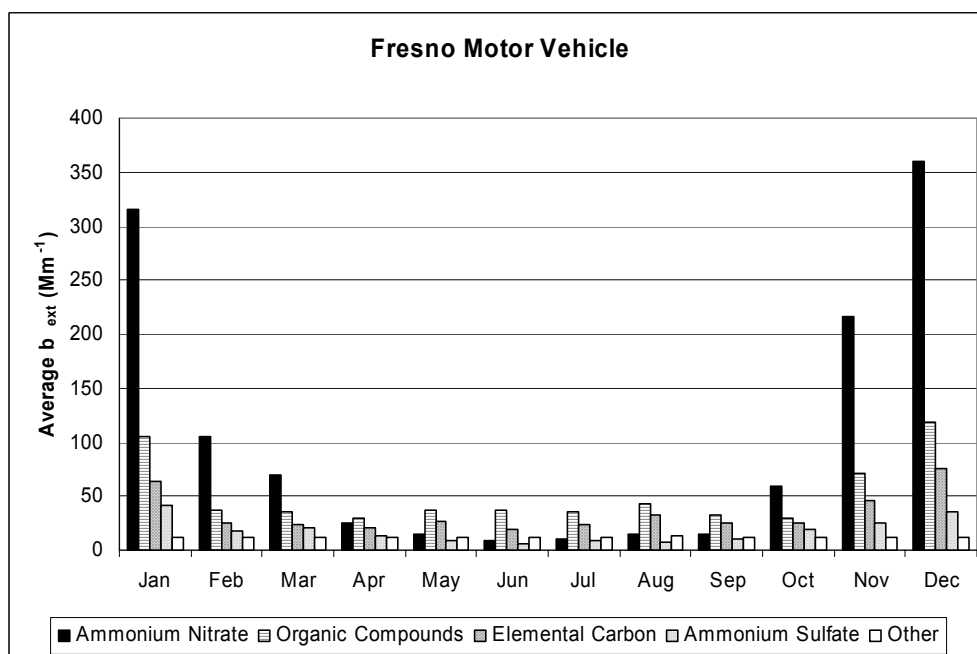
**Figure 3-43. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Modesto**



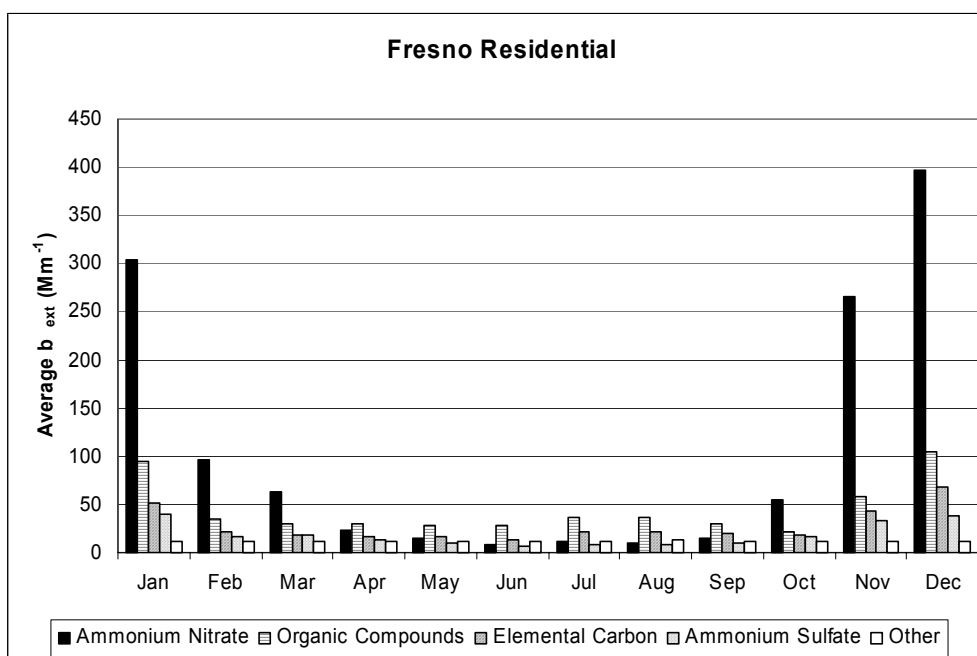
**Figure 3-44. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Merced**



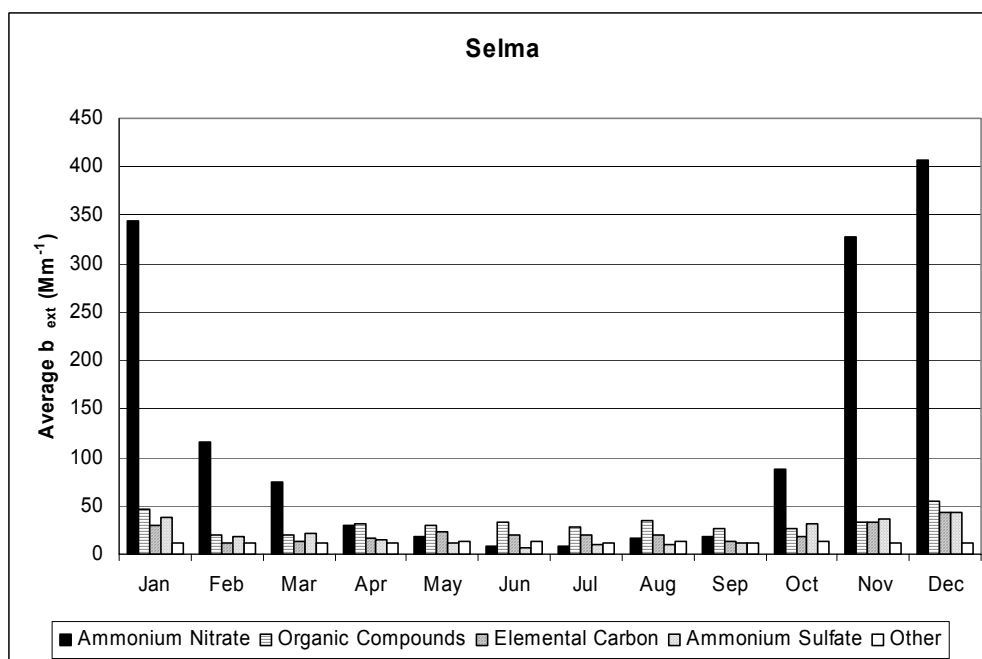
**Figure 3-45. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Fresno First Street**



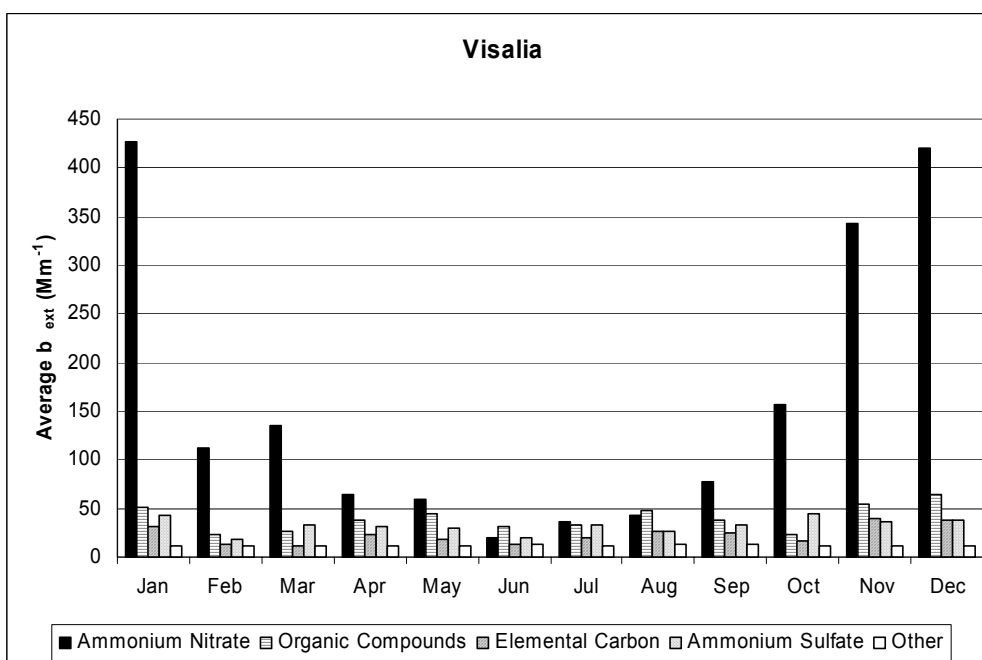
**Figure 3-46. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Fresno Motor Vehicle**



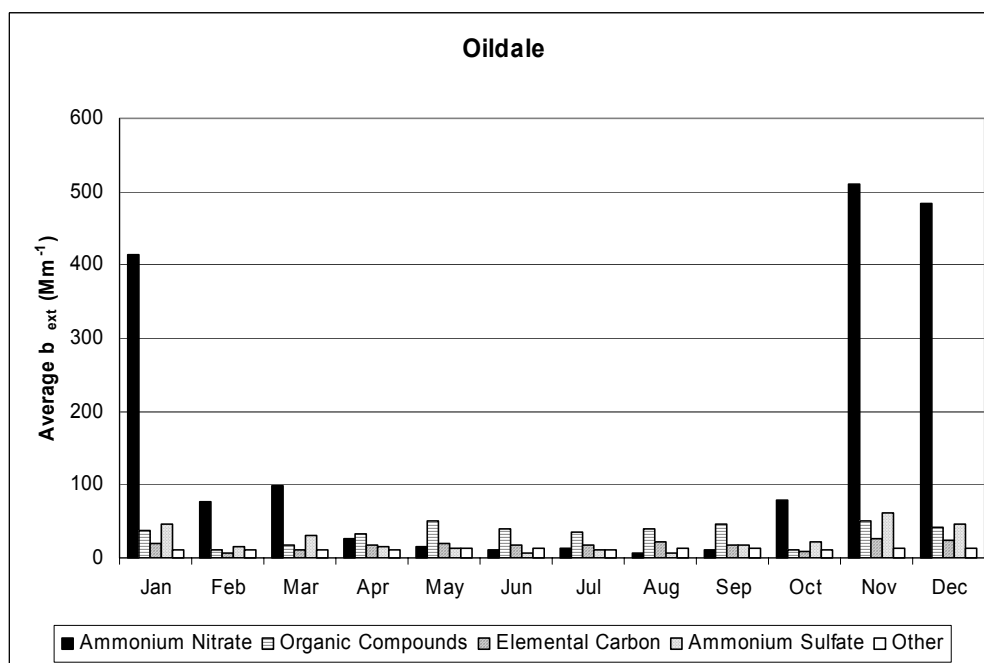
**Figure 3-47. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Fresno Residential**



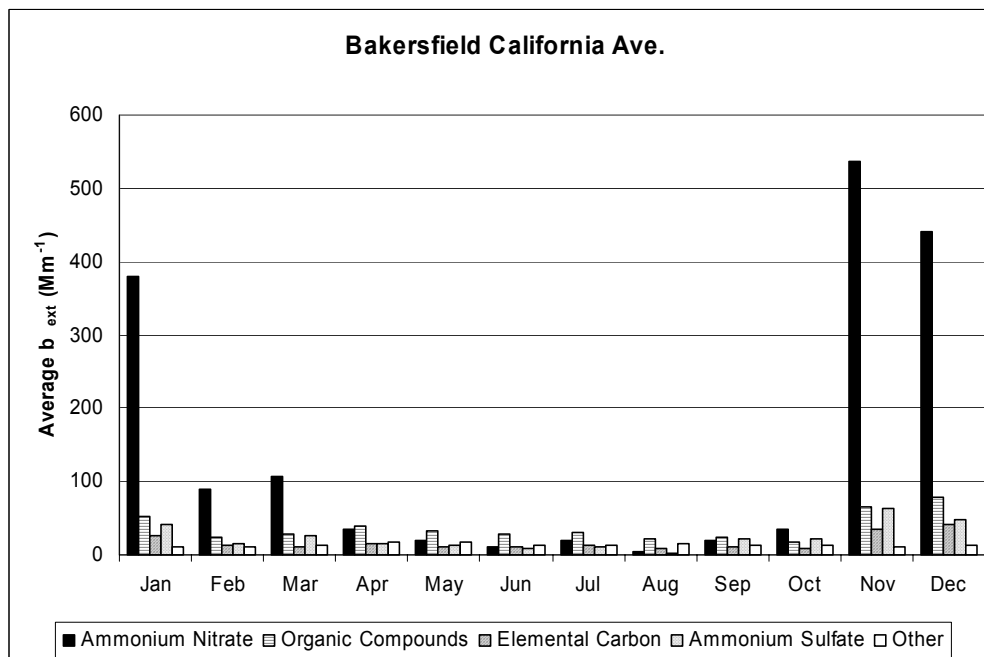
**Figure 3-48. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Selma**



**Figure 3-49. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Visalia**

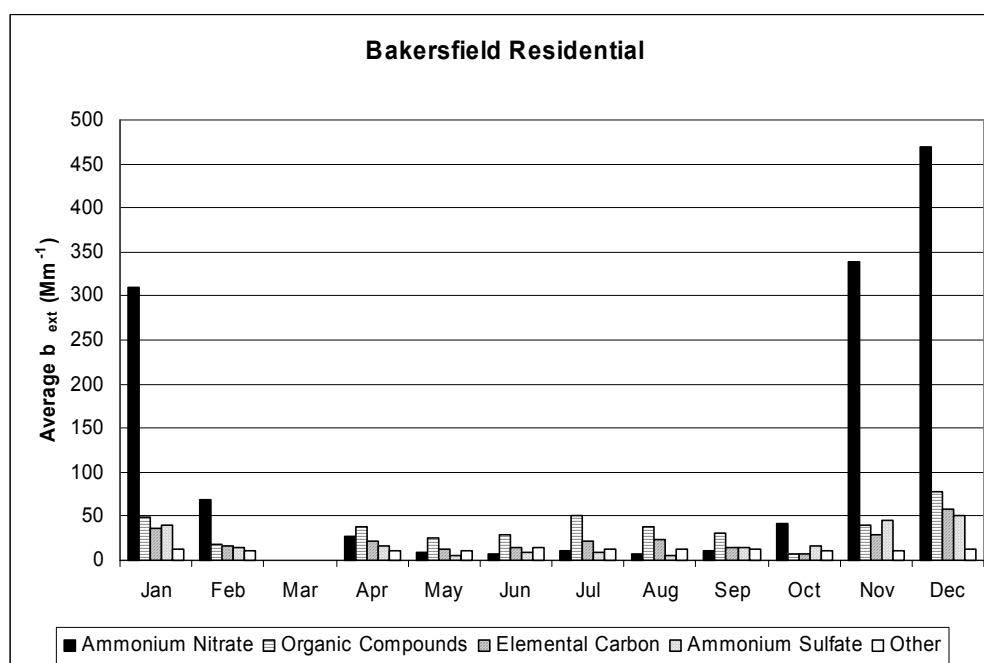


**Figure 3-50. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Oildale**



**Figure 3-51. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Bakersfield California Avenue**





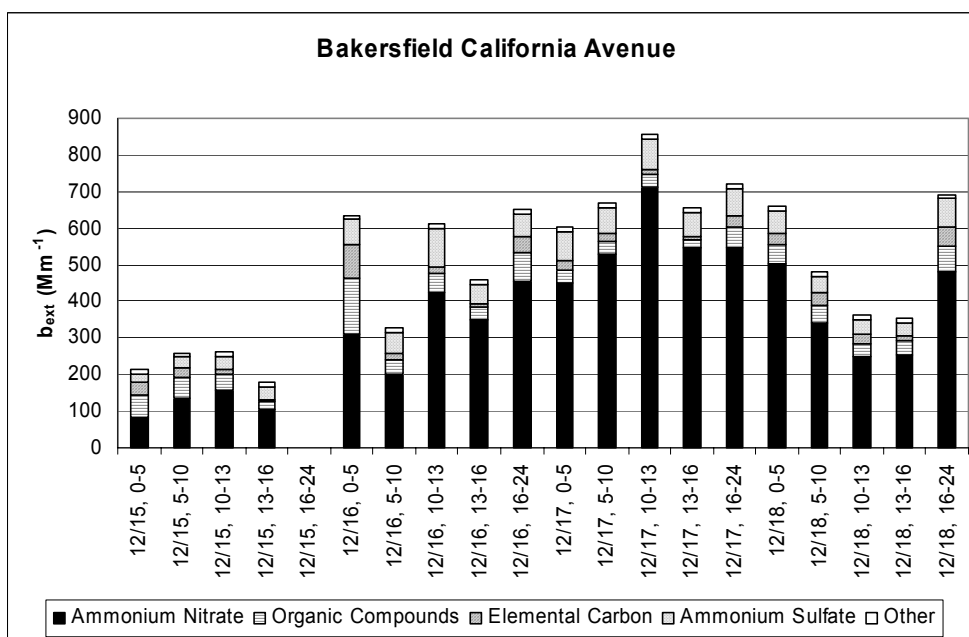
**Figure 3-52. Average Chemical Constituent Contributions to the Light Extinction Coefficient by Month for Bakersfield Residential**

### 3.5 When and How Long During the Day Do Individual Constituents Contribute to the Light Extinction Coefficient?

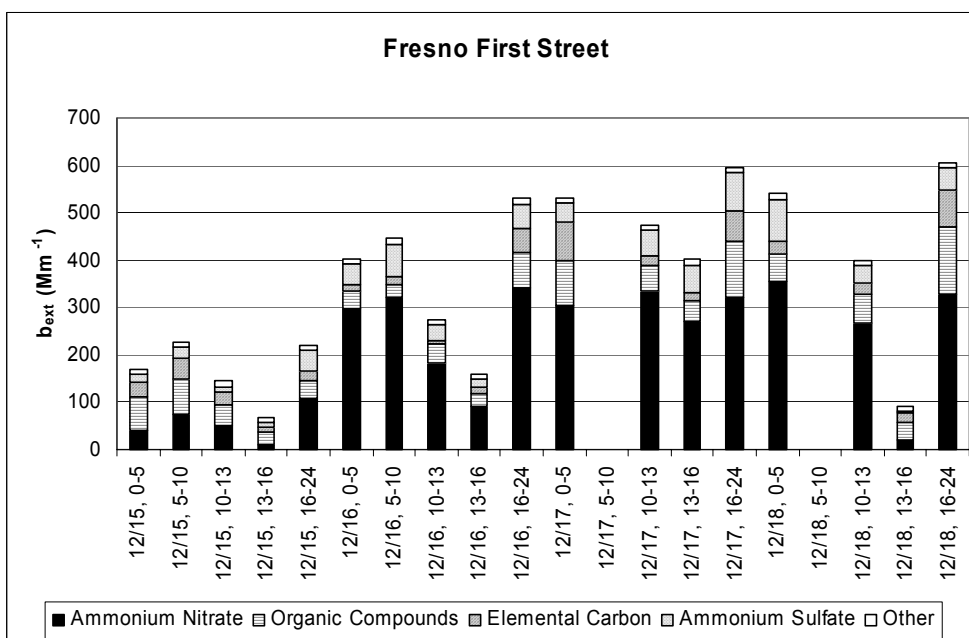
As discussed previously in Section 3.1, the light extinction efficiencies were applied to chemical composition data from the five PM<sub>2.5</sub> samples collected daily at the Bakersfield California Avenue, Fresno First Street and Angiola sites during the four intensive operational periods. These calculations were not made for sampling periods when the relative humidity was always above 95 percent. Relative humidity at Angiola exceeded 95 percent throughout several sampling periods during the first and second IOP. Additionally, relative humidity data from Angiola were missing for several sampling periods during the second IOP and during the entire fourth IOP. Therefore, results from Angiola are only presented for the third IOP.

#### 3.5.1 Chemical Constituent Contributions to the Light Extinction Coefficient During the First Intensive Operational Period (12/15/00-12/18/00)

Chemical constituent contributions during the first IOP are shown in Figures 3-53 and 3-54 for the Bakersfield and Fresno sites, respectively. The missing period at Bakersfield in Figure 3-53 was caused by an invalid PM<sub>2.5</sub> sample. Relative humidity at Fresno was above 95 percent during the missing periods in Figure 3-54.



**Figure 3-53. Chemical Constituent Contributions to the Light Extinction Coefficient During the First IOP at the Bakersfield California Avenue Site**

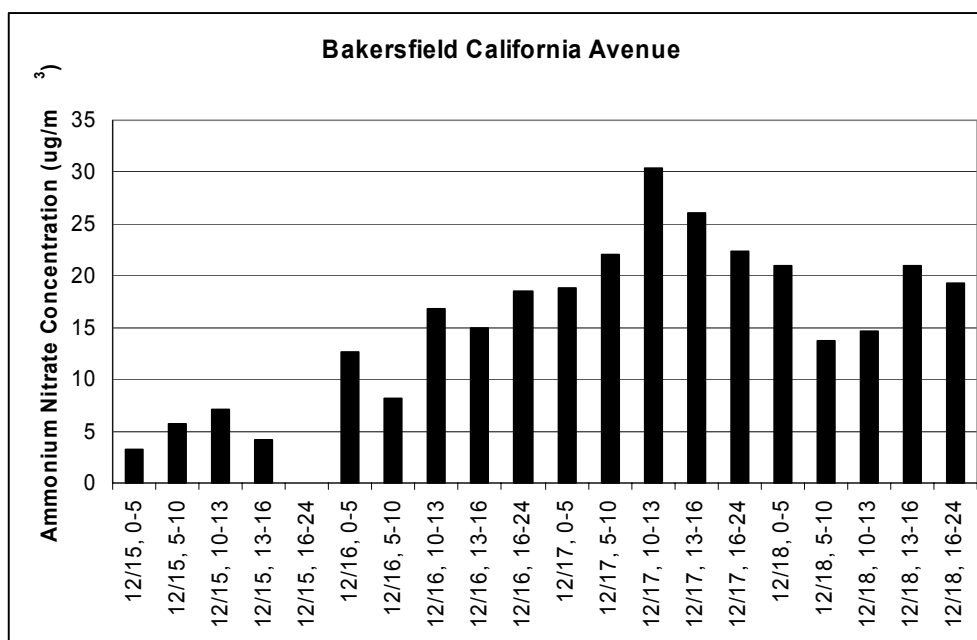


**Figure 3-54. Chemical Constituent Contributions to the Light Extinction Coefficient During the First IOP at the Fresno First Street Site**

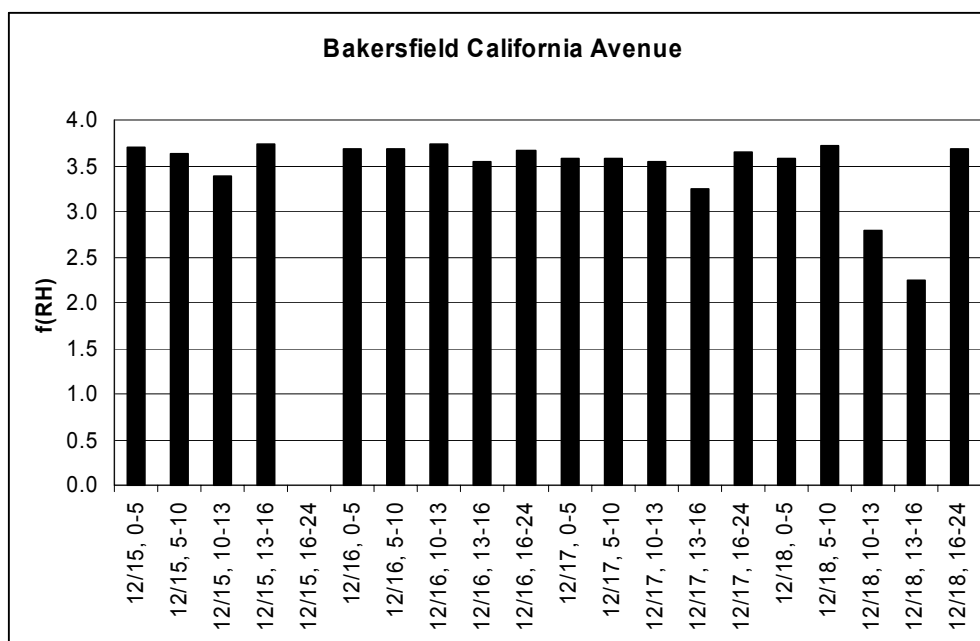
There was not a consistent diurnal pattern in the light extinction coefficient or in the constituent contributions at Bakersfield. Instead, there was a general increase from the 0500-1000 sample on December 16, 2000 to the 100-1300 sample on December 17, 2000, followed by a general decrease through the 1300-1500 sample on December 18, 2000. In contrast, the light extinction coefficient and constituent contributions at Fresno were lower for the daytime (1000-1300 and 1300-1600) samples than for the other samples during each of the three days.

Ammonium nitrate concentrations and values of  $f(RH)$  at Bakersfield are shown in Figures 3-55 and 3-56, respectively. As seen in Figure 3-56,  $f(RH)$  did not vary substantially at Bakersfield, with the exception of the 1000-1300 and 1300-1600 periods on December 18. As a result, period-to-period variations in the light extinction coefficient tracked variations in ammonium nitrate concentrations through the 0500-1000 sampling period on December 18. Because of the decreases  $f(RH)$  during next two sampling periods, the light extinction coefficient decreased from the previous period, although the ammonium nitrate concentration increased.

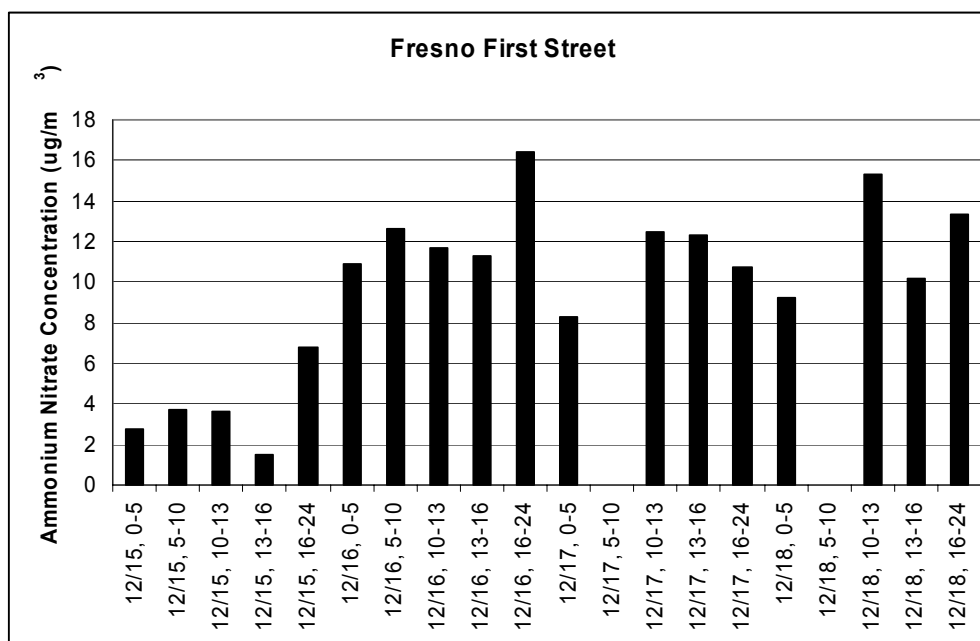
Ammonium nitrate concentrations and  $f(RH)$  at Fresno are shown in Figures 3-57 and 3-58, respectively. In contrast with the behavior at Bakersfield,  $f(RH)$  was consistently lower during the 1000-1300 and 1300-1600 periods every day, which caused the lower daytime light extinction coefficient.



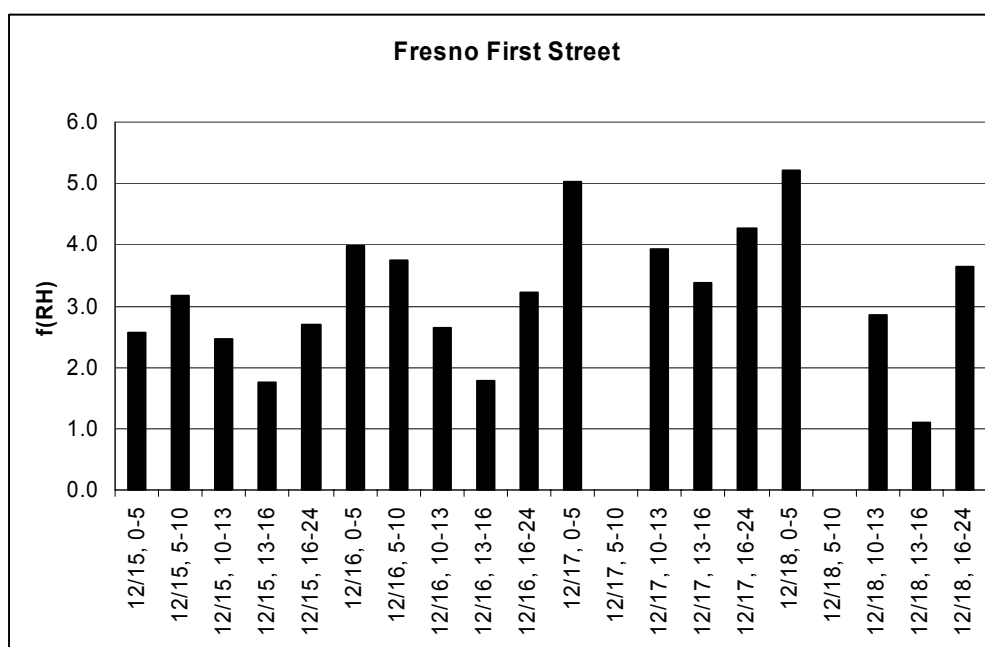
**Figure 3-55. Ammonium Nitrate Concentrations at the Bakersfield California Avenue Site During the First IOP**



**Figure 3-56. f(RH) at the Bakersfield California Avenue Site During the First IOP**



**Figure 3-57. Ammonium Nitrate Concentrations at the Fresno First Street Site During the First IOP**

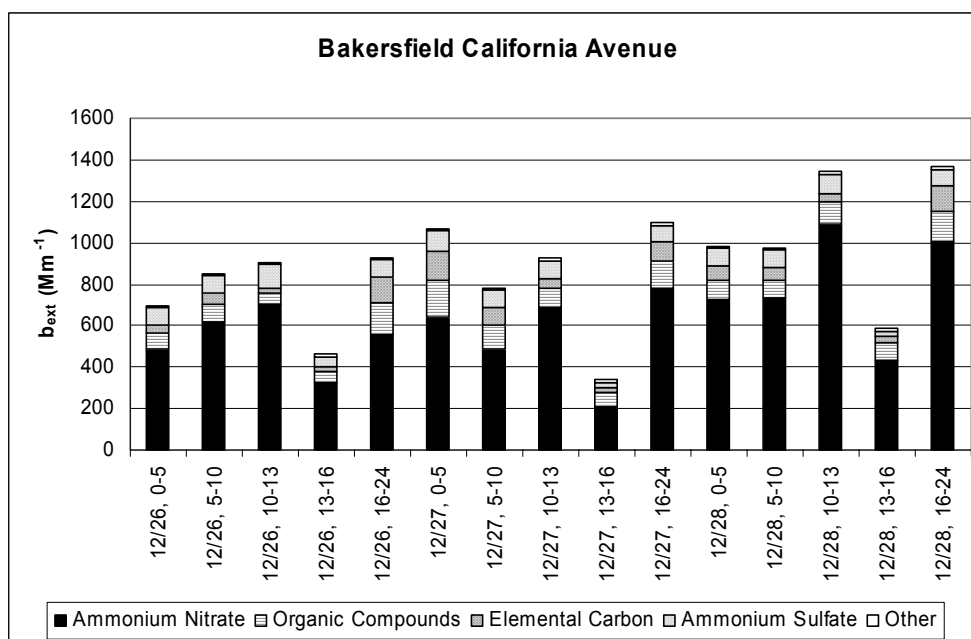


**Figure 3-58. f(RH) at the Fresno First Street Site During the First IOP**

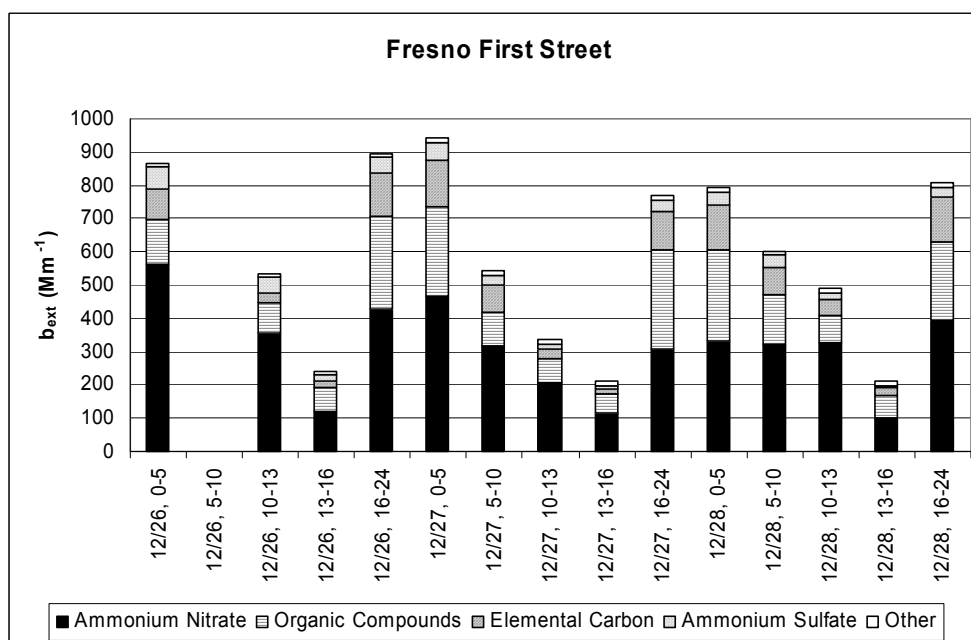
### **3.5.2 Chemical Constituent Contributions to the Light Extinction Coefficient During the Second Intensive Operational Period (12/26/00-12/28/00)**

Chemical constituent contributions during the second IOP are shown in Figures 3-59 and 3-60 for the Bakersfield and Fresno sites, respectively. In contrast with the first IOP, the light extinction coefficient and the ammonium nitrate contribution at Bakersfield were consistently lower during the 1300-1600 sampling period than during the other periods of the day. The light extinction coefficient was also consistently lower during the day at Fresno than during the other periods. Additionally, organic compounds plus elemental carbon contributed more than ammonium nitrate at Fresno during the 0000-0500 and 1600-2400 periods.

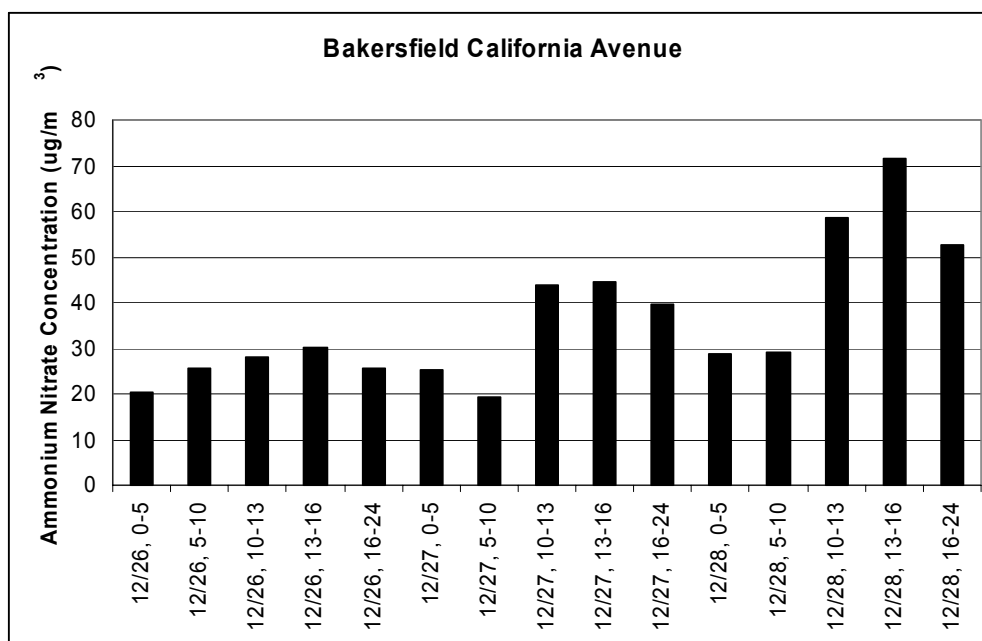
Ammonium nitrate concentrations and f(RH) at Bakersfield are shown in Figures 3-61 and 3-62, respectively. As seen in Figure 3-61, the ammonium nitrate concentration was higher during the 1000-1300 and 1300-1600 periods on December 27 and 28 than during the other periods on those days. However, as seen in Figure 3-62, f(RH) was lower during these periods, which caused the relatively low values of the light extinction coefficient and the ammonium nitrate contribution.



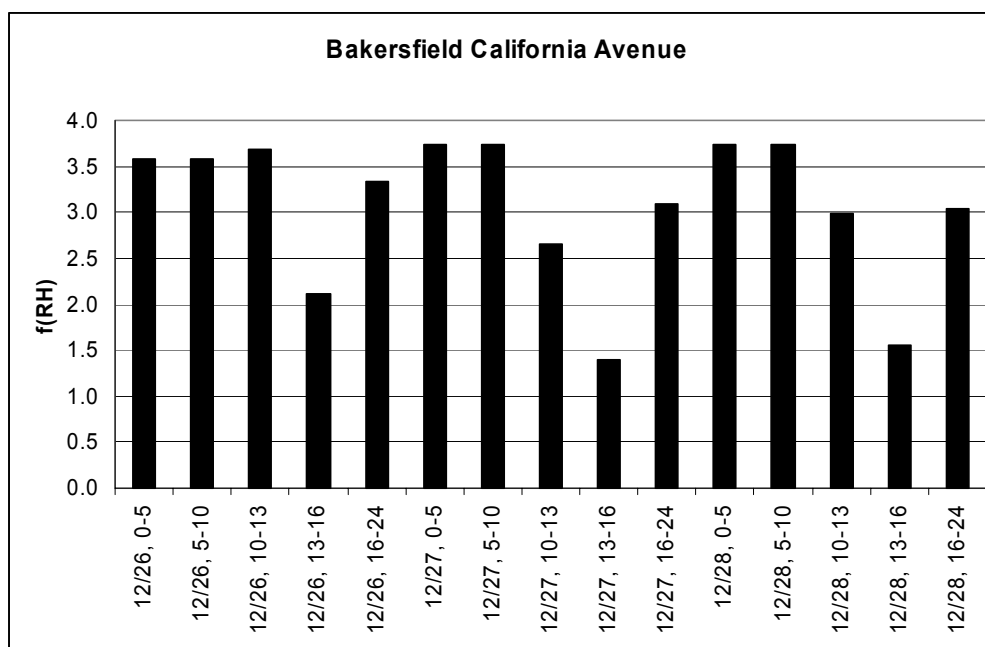
**Figure 3-59. Chemical Constituent Contributions to the Light Extinction Coefficient During the Second IOP at the Bakersfield California Avenue Site**



**Figure 3-60. Chemical Constituent Contributions to the Light Extinction Coefficient During the Second IOP at the Fresno First Street Site**

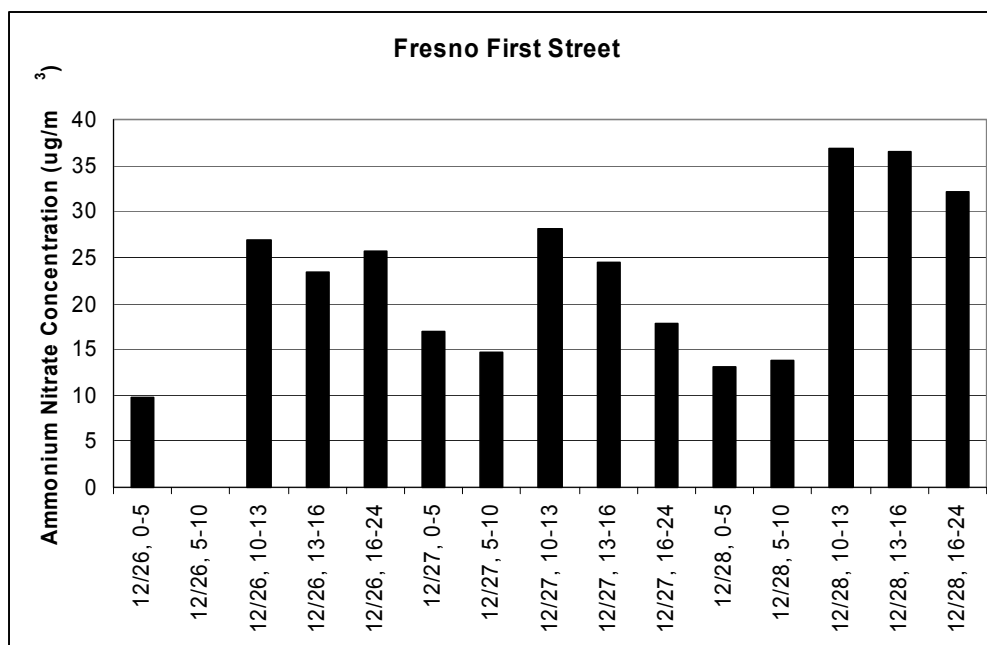


**Figure 3-61. Ammonium Nitrate Concentrations at the Bakersfield California Avenue Site During the Second IOP**



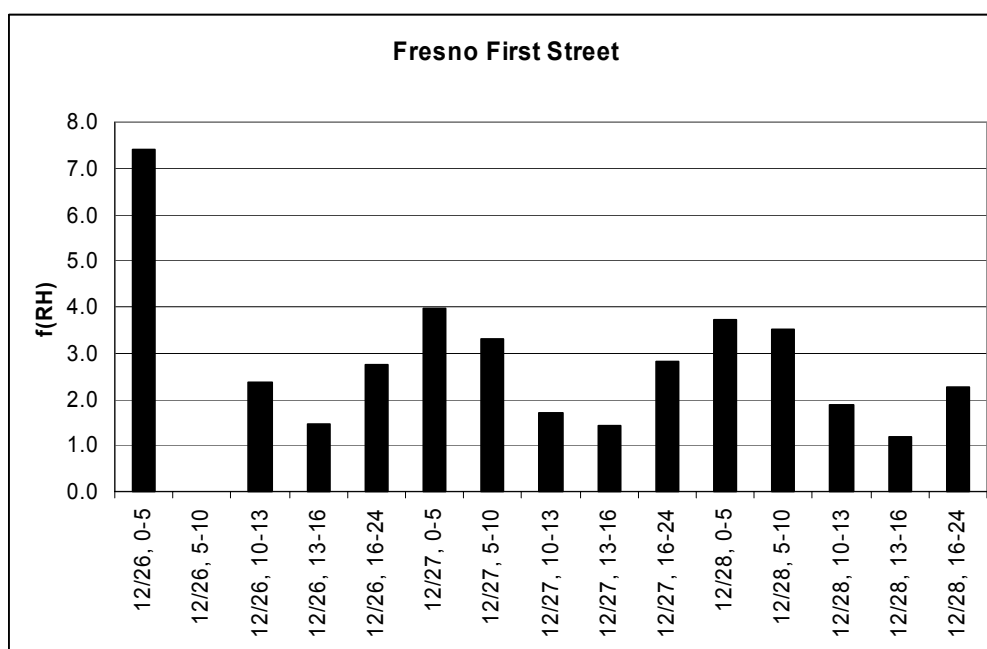
**Figure 3-62. f(RH) at the Bakersfield California Avenue Site During the Second IOP**

Ammonium nitrate concentrations and  $f(RH)$  at Fresno are shown in Figures 3-63 and 3-64, respectively. The patterns at Fresno were similar to those at Bakersfield: the ammonium nitrate concentration was higher during the daytime (1000-1300 and 1300-1600) sampling periods than during the rest of the day on December 27 and 28, but  $f(RH)$  and the resulting ammonium nitrate contribution to the light extinction coefficient were lower.



**Figure 3-63. Ammonium Nitrate Concentrations at the Fresno First Street Site During the Second IOP**

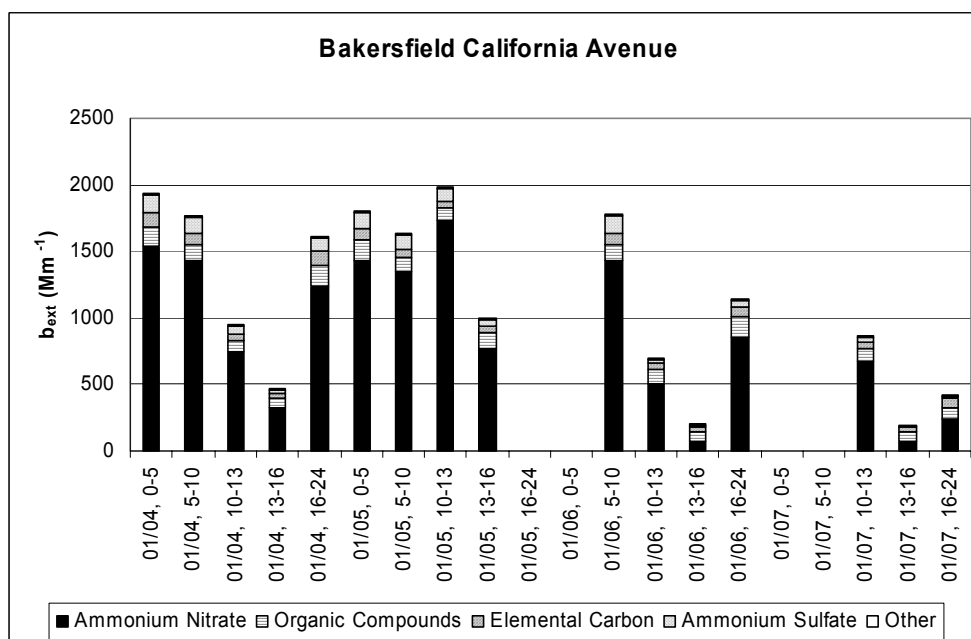




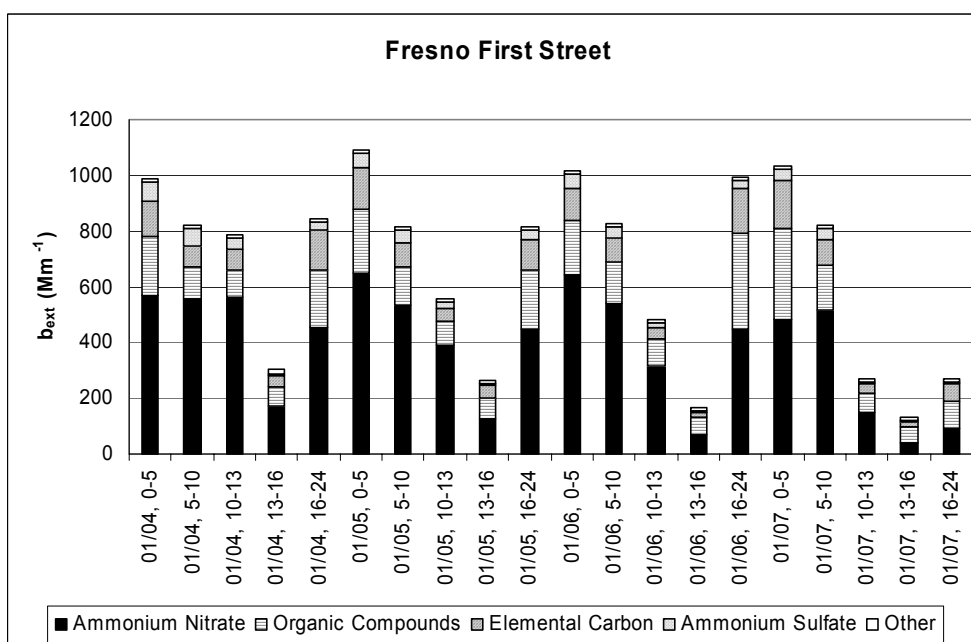
**Figure 3-64. f(RH) at the Fresno First Street Site During the Second IOP**

### **3.5.3 Chemical Constituent Contributions to the Light Extinction Coefficient During the Third Intensive Operational Period (1/4/01-1/7/01)**

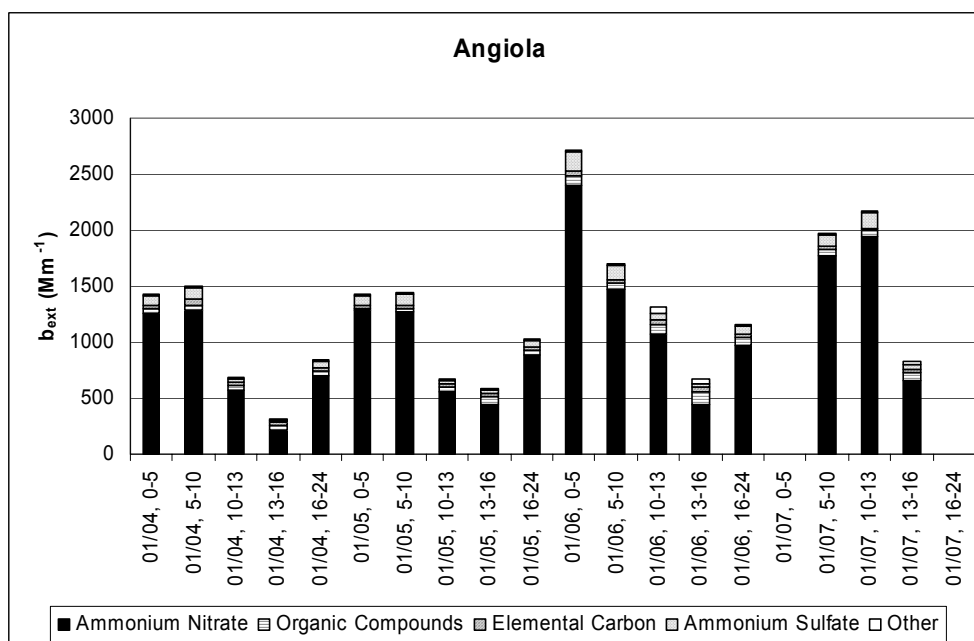
Chemical constituent contributions during the third IOP are shown in Figures 3-65, 3-66 and 3-67 for the Bakersfield, Fresno and Angiola sites, respectively. The gaps for Bakersfield in Figure 3-65, which were caused by missing PM<sub>2.5</sub> data, make it difficult to evaluate the consistency of diurnal patterns. However, the available data seem to show that the light extinction coefficient was generally lower during the 1300-1600 period than during the rest of the day. The diurnal patterns at Fresno were similar to the patterns during the second IOP, with the light extinction coefficient and ammonium nitrate contribution lower during the daytime periods than during the other periods. The contributions from organic compounds and elemental carbon relative to ammonium nitrate were also generally higher during the nighttime periods than during the daytime periods. The light extinction coefficient at Angiola tended to be higher during the 0000-0500 and 0500-1000 sampling periods than during the rest of the day, with ammonium nitrate accounting for almost all of the light extinction during all periods.



**Figure 3-65. Chemical Constituent Contributions to the Light Extinction Coefficient During the Third IOP at the Bakersfield California Avenue Site**



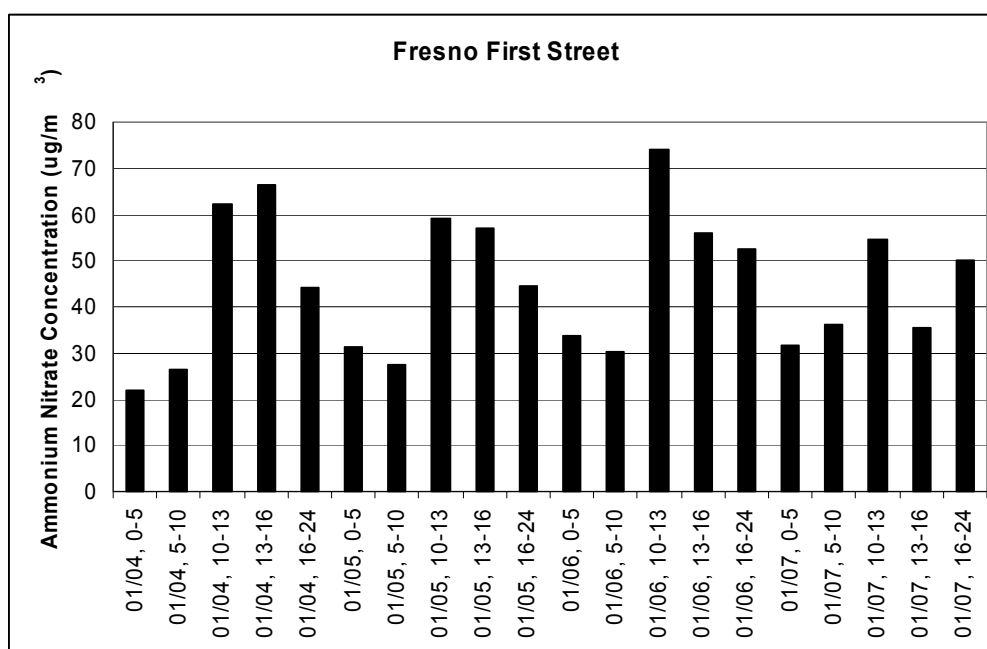
**Figure 3-66. Chemical Constituent Contributions to the Light Extinction Coefficient During the Third IOP at the Fresno First Street Site**



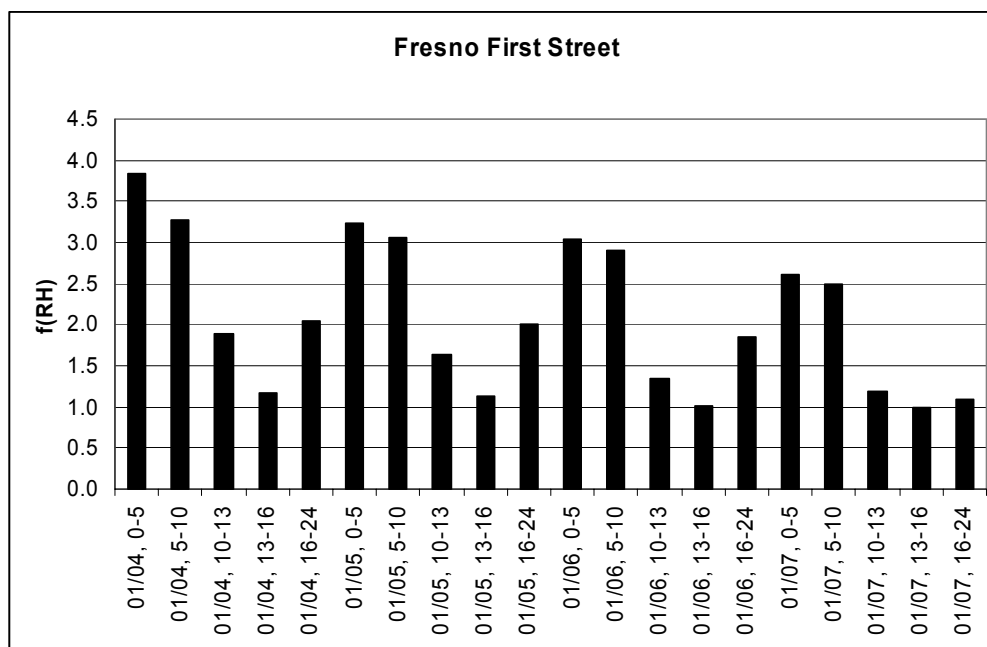
**Figure 3-67. Chemical Constituent Contributions to the Light Extinction Coefficient During the Third IOP at the Angiola Site**

Ammonium nitrate concentrations and  $f(RH)$  at Fresno are shown in Figures 3-68 and 3-69, respectively. The patterns were similar to those at Fresno during the second IOP, with ammonium nitrate concentrations higher during the daytime (1000-1300 and 1300-1600) sampling periods than during the rest of the day and  $f(RH)$  and the resulting ammonium nitrate contribution to the light extinction coefficient lower.

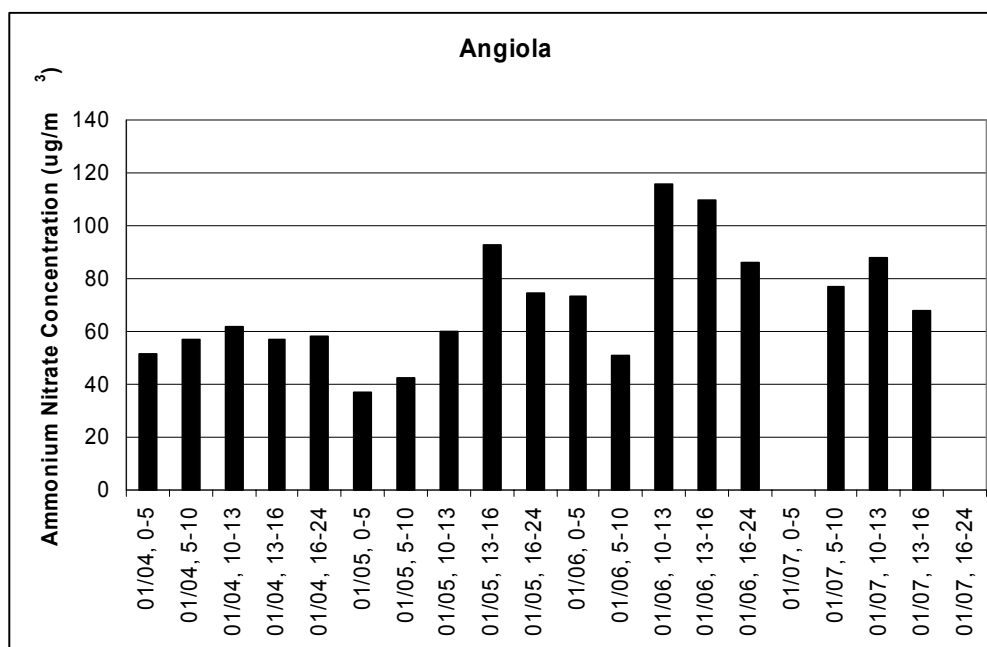
Ammonium nitrate concentrations and  $f(RH)$  at Angiola are shown in Figures 3-70 and 3-71, respectively. Ammonium nitrate concentrations tended to be higher during the daytime than during other sampling periods, but  $f(RH)$  was lower during the daytime, which led to generally lower ammonium nitrate contributions to the light extinction coefficient during the day.



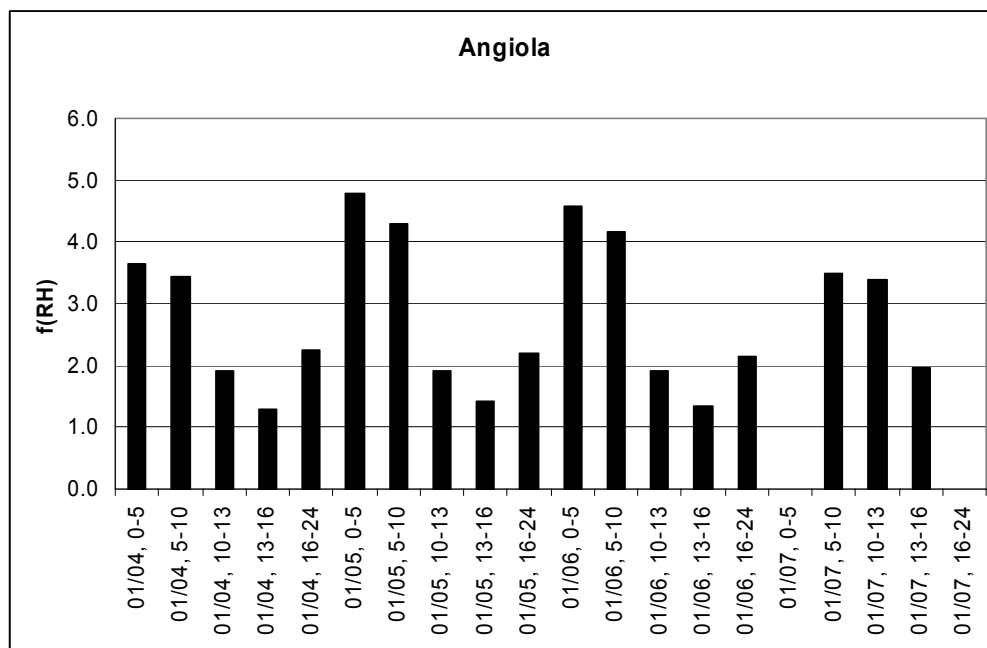
**Figure 3-68. Ammonium Nitrate Concentrations at the Fresno First Street Site During the Third IOP**



**Figure 3-69. f(RH) at the Fresno First Street Site During the Third IOP**



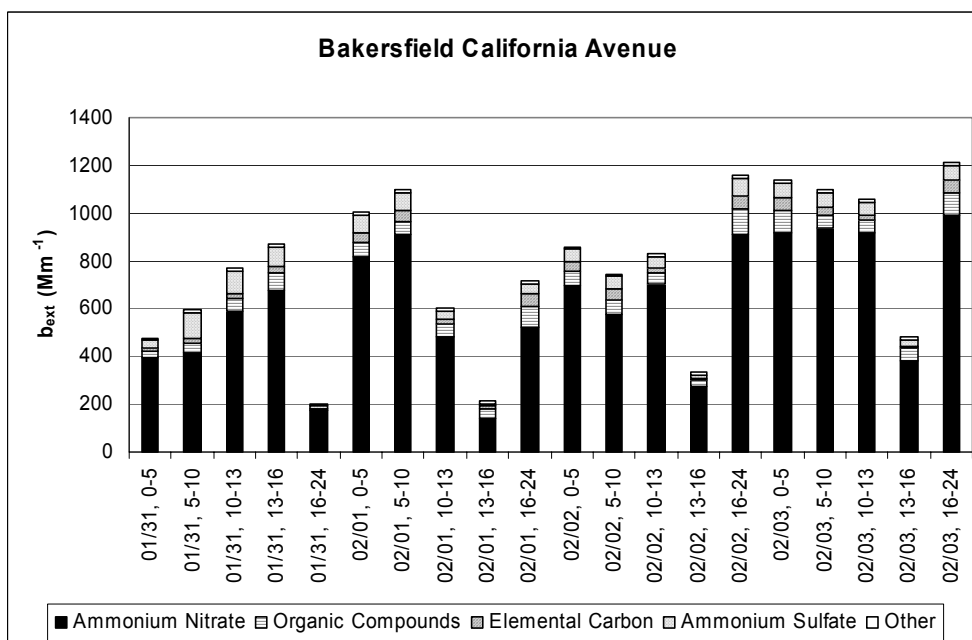
**Figure 3-70. Ammonium Nitrate Concentrations at the Angiola Site During the Third IOP**



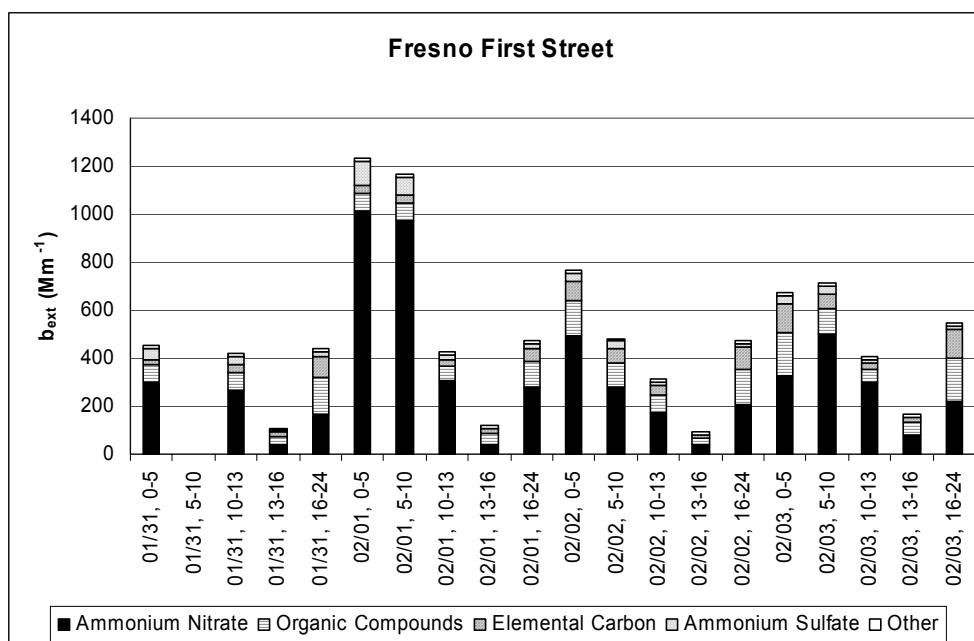
**Figure 3-71. f(RH) at the Angiola Site During the Third IOP**

### 3.5.4 Chemical Constituent Contributions to the Light Extinction Coefficient During the Fourth Intensive Operational Period (1/31/01-2/3/01)

Chemical constituent contributions during the fourth IOP are shown in Figures 3-72 and 3-73 for the Bakersfield and Fresno sites, respectively. The light extinction coefficient and the ammonium nitrate contribution at Bakersfield were consistently lower during the 1300-1600 sampling period than during the other periods of the day on three of the four days, but higher than during the rest of the day on the first day of the IOP. The diurnal patterns at Fresno were similar to the patterns during the second and third IOPs, with the light extinction coefficient consistently lower during the day than during the other periods. Additionally, organic compounds plus elemental carbon were substantial contributors to the light extinction coefficient during the 0000-0500 and 1600-2400 periods on two of the four days.



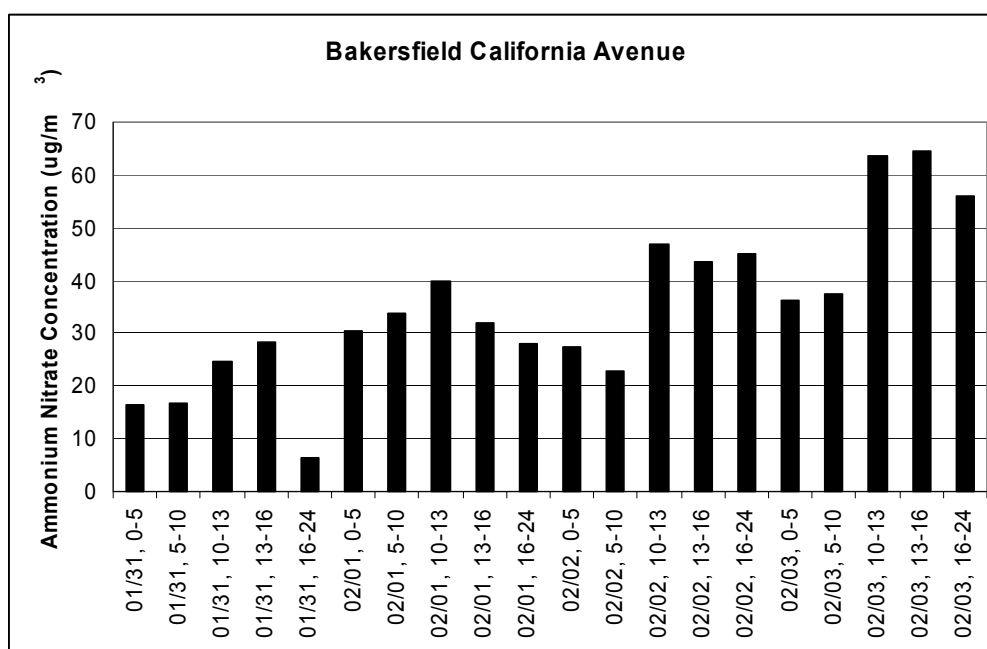
**Figure 3-72. Chemical Constituent Contributions to the Light Extinction Coefficient During the Fourth IOP at the Bakersfield California Avenue Site**



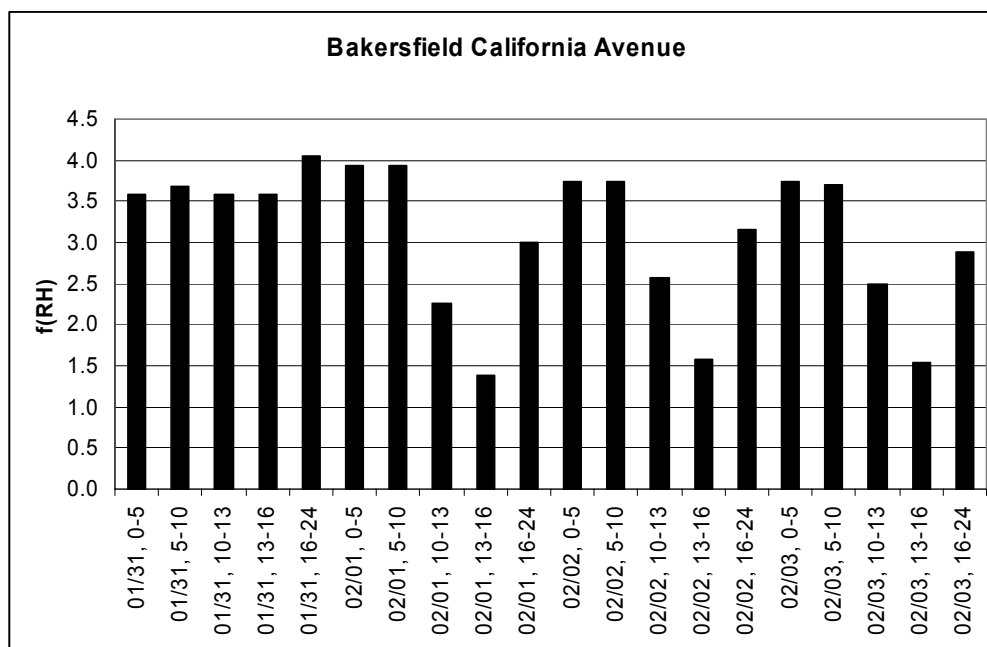
**Figure 3-73. Chemical Constituent Contributions to the Light Extinction Coefficient During the Fourth IOP at the Fresno First Street Site**

Ammonium nitrate concentrations and  $f(RH)$  at Bakersfield are shown in Figures 3-74 and 3-75, respectively. Ammonium nitrate concentrations were generally higher during daytime sampling periods, including the 0500-1000 period, than during the nighttime periods.  $f(RH)$  was fairly constant and high (above 3.5) from the beginning of the IOP on January 31 through the 0500-1000 period on February 1. As a result, the ammonium nitrate contribution to the light extinction coefficient followed the ammonium nitrate concentration during this beginning portion of the IOP.  $f(RH)$  tended to be lower during the 1000-1300 and 1300-1600 periods during the rest of the IOP. The low value during the 1300-1600 period led to lower ammonium nitrate contributions to the light extinction coefficient during the 1300-1600 period than during other periods of the day. However, high ammonium nitrate concentrations occurred during the 1000-1300 period, which resulted in relatively high ammonium nitrate contributions to the light extinction coefficient.

Ammonium nitrate concentrations and  $f(RH)$  at Fresno are shown in Figures 3-76 and 3-77, respectively. The patterns were similar to those at Fresno during the second and third IOPs, with ammonium nitrate concentrations higher during the daytime (1000-1300 and 1300-1600) sampling periods than during the rest of the day and  $f(RH)$  and the resulting ammonium nitrate contribution to the light extinction coefficient lower.

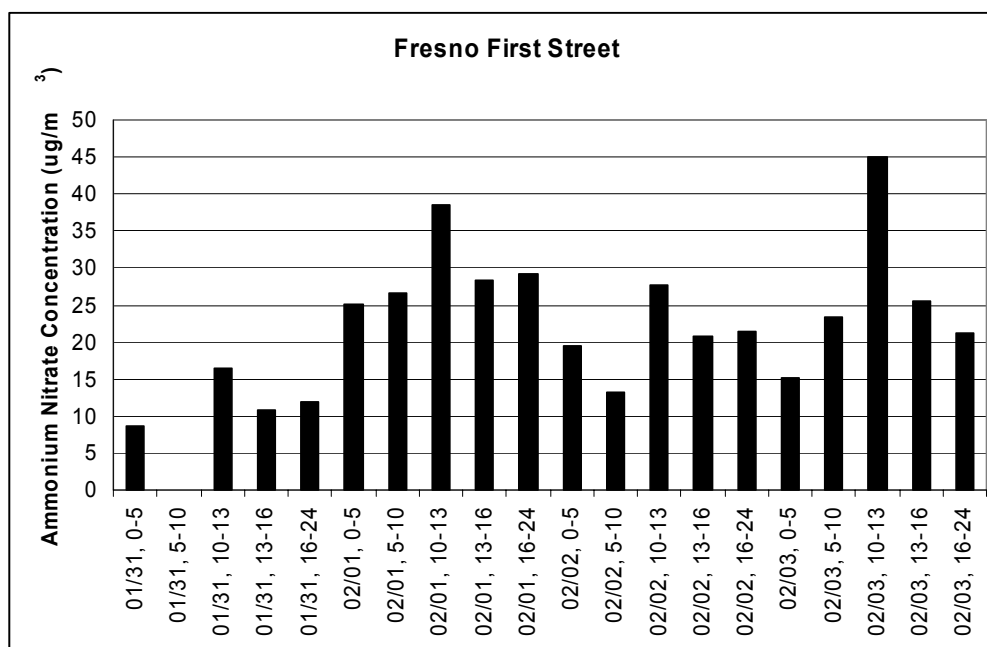


**Figure 3-74. Ammonium Nitrate Concentrations at the Bakersfield California Avenue Site During the Fourth IOP**

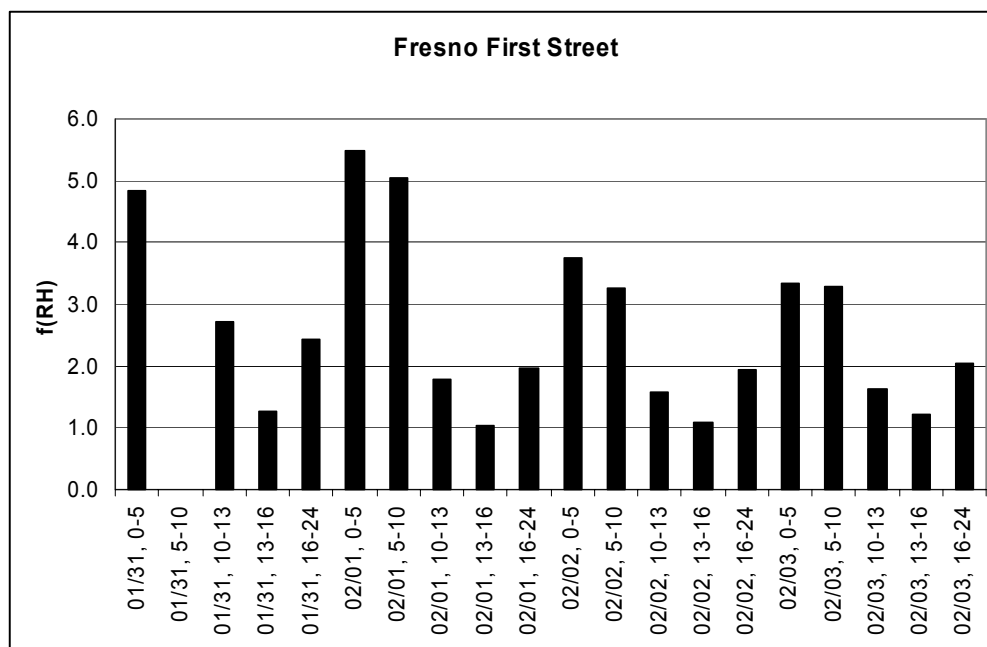


**Figure 3-75. f(RH) at the Bakersfield California Avenue Site During the Fourth IOP**





**Figure 3-76. Ammonium Nitrate Concentrations at the Fresno First Street Site During the Fourth IOP**



**Figure 3-77. f(RH) at the Fresno First Street Site During the Fourth IOP**

## 4.0 SUMMARY

The evaluation of light scattering efficiencies developed previously for IMS95 (McDade, 1997) and the IMPROVE program (Sisler and Malm, 2000) for use in the current work indicated that these light scattering efficiencies under-predicted the measured light scattering coefficient at high values. An empirically derived adjustment to the IMPROVE ammonium nitrate and ammonium sulfate light scattering relative humidity dependence [ $f(RH)$ ] improved the agreement.

Fairly good agreement was found between light scattering coefficients calculated using the IMPROVE efficiencies with the adjusted  $f(RH)$  and values measured using nephelometers with heaters at 10 non-Mojave Desert sites. However, agreement between calculated and measured values was poor at three Mojave Desert sites. The sum of the chemical constituent concentrations frequently exceeded the measured  $PM_{2.5}$  mass concentration at these sites, which suggests that problems with the chemical composition measurements caused the poor agreement between the calculated and measured light scattering coefficients. Therefore, chemical constituent contributions to the light extinction coefficient at Mojave Desert sites were not estimated.

Results from applying the IMPROVE light extinction efficiencies with the adjusted  $f(RH)$  to 24-hour average data collected from December 1999 through January 2001 at 12 CRPAQS sites and to shorter duration data collected at three CRPAQS sites between mid-December 2000 and early February 2001 were examined to address the following questions.

### **Where, how much and how often do individual constituents contribute to the light extinction coefficient?**

This question was addressed separately for days with high, low and intermediate 24-hour average light extinction. High and low light extinction days were defined as the days with the 20 percent highest and 20 percent lowest calculated light extinction coefficient at each site., and intermediate light extinction days were defined as the other 60 percent of the days.

The calculated light extinction coefficient, averaged over the 20 percent highest days, ranged from a little over  $400 \text{ Mm}^{-1}$  at Sacramento, which was substantially lower than the other sites, to about  $900 \text{ Mm}^{-1}$  at Oildale. Ammonium nitrate was the largest contributor at all sites, contributing from about  $240 \text{ Mm}^{-1}$  at Sacramento to about  $740 \text{ Mm}^{-1}$  at Oildale. Elevated values of the ammonium nitrate light scattering coefficient were caused by high ammonium nitrate concentrations and high relative humidity. Organic compounds were the second largest contributor at all sites and contributed more at the three Fresno sites than at the other sites. Water associated with ammonium nitrate contributed more than 60 percent of the average calculated light extinction coefficient at every site and more than 80 percent at Oildale. The percentage was lower at Sacramento and the three Fresno sites than at the other sites. Ammonium nitrate almost always

contributed more than half of the 24-hour average calculated light extinction on individual days and frequently contributed more than 70 percent.

Associations between high values of the light extinction coefficient and exceedances of the 24-hour  $\text{PM}_{2.5}$  NAAQS were also examined. The purpose of this examination was to evaluate whether or not elevated values of the light extinction coefficient were always associated with  $\text{PM}_{2.5}$  mass concentrations that exceeded the NAAQS of  $65 \mu\text{g}/\text{m}^3$ . The measured  $\text{PM}_{2.5}$  mass concentration was above the NAAQS on less than half of the days with the 20 percent highest light extinction coefficient at the northern sites (Sacramento, Stockton, Modesto and Merced), while it was above the NAAQS on more than half the days at the southern sites (the three Fresno sites, Selma, Visalia, Oildale and the two Bakersfield sites). The average calculated light extinction coefficient was 1.9 to 2.5 times higher at the northern sites when the NAAQS was exceeded than when it was not. At most of the more southern sites, the calculated light extinction coefficient was less than twice as high when the NAAQS was exceeded than when it was not. Thus, the NAAQS was not exceeded on some days with poor visibility at all of the sites, but the frequency of poor visibility on these days varied by site.

The calculated light extinction coefficient, averaged over the middle 60 percent days, ranged from about  $100 \text{ Mm}^{-1}$  at Sacramento to about  $225 \text{ Mm}^{-1}$  at Visalia. Ammonium nitrate was the largest contributor on average during these days, but organic compounds accounted for more of the calculated light extinction than during the 20 percent highest light extinction days. Water accounted for more than 40 percent of the calculated light extinction coefficient at all sites and over 60 percent of the light extinction coefficient at Visalia. Ammonium nitrate was the only constituent that accounted for more than half the 24-hour average light extinction coefficient on more than one or two individual days at any site.

The calculated light extinction coefficient, averaged over the 20 percent lowest days, ranged from about  $55 \text{ Mm}^{-1}$  at Sacramento and one of the Fresno sites to about  $100 \text{ Mm}^{-1}$  at Visalia. Organic compounds were the largest contributor at all sites, but ammonium nitrate was a major contributor at some sites, particularly Stockton, Modesto, Merced and Visalia. Water accounted for less than 25 percent of the calculated light extinction coefficient at many sites and no more than 40 percent at any site. None of the constituents contributed more than half of the 24-hour average light extinction coefficient on more than a few days at any site. Organic compounds accounted for more than 25 percent of the 24-hour average light extinction coefficient on 40 percent to 100 percent of the days.

### **How does the light extinction coefficient vary during the year?**

The highest 24-hour average values of the light extinction coefficient during the year occurred during January, November and December at all sites, although low values also occurred during these months. High values also occurred during October at the Fresno and Visalia sites. The calculated light extinction coefficient was generally low from April through September.

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**When during the year do individual constituents contribute to the light extinction coefficient?**

Monthly average ammonium nitrate contributions were higher during January, February, November and December than during other months at all sites. The highest average contributions from organic compounds also occurred during January, November and December, particularly at Sacramento and the Fresno sites. Ammonium nitrate was the largest contributor to the monthly average light extinction coefficient during January, November and December at all sites as well as during March and October at some sites. Organic compounds were the largest contributor at most sites from April through September.

**When and how long during the day do individual constituents contribute to the light extinction coefficient?**

The light extinction coefficient during the Intensive Operational Periods was usually highest during the nighttime sampling periods (1600-2400 and 0000-0500) and lowest during the afternoon sampling period (1300-1600), although the calculated light extinction coefficient remained high throughout the day at times at Bakersfield. Ammonium nitrate was the largest contributor during all sampling periods at Bakersfield and Angiola, while organic compounds plus elemental carbon were often the largest contributor at Fresno, particularly during the nighttime periods. Although the ammonium nitrate concentration was frequently higher during the morning (1000-1600) and afternoon sampling periods than at night, lower relative humidity during the afternoon than at night frequently led to low afternoon contributions to the light extinction coefficient.

## 5.0 REFERENCES

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- McDade, C. (1997). Contributions of chemical constituents to visibility reduction, contributions of chemical constituents to light extinction budget, and contributions of emissions sources to light extinction budget. Report No. 97-7PM. Prepared for California Air Resources Board, Sacramento, CA, by ENSR, Inc., Camarillo, CA.
- Sisler, J.F. and Malm, W.C. (2000). Interpretation of trends of  $PM_{2.5}$  and reconstructed visibility from the IMPROVE network. JAWMA 50, 775-789.
- Watson, J.G. (2005) Personal communication between John Watson, Desert Research Institute, and Karen Magliano, California Air Resources Board.